Trace metals in soils irrigated with waste water in a periurban area downstream Hanoi City, Vietnam

Josef Bjuhr

Handledare: Prof Ingrid Öborn
Prof Ingvar Nilsson

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Sveriges lantbruksuniversitet
Institutionen för markvetenskap
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Abstract

The rapid urbanization and industrialisation in many South-East Asian countries has resulted in increasing amounts of untreated industrial and domestic waste water, which is discharged into rivers and lakes. The waste water is a highly complex and nutrient rich water solution used by the farmers for irrigation of their fields. It contains various potentially toxic elements including several trace metals. A better understanding of the irrigation systems used, and the distribution of the metals across arable fields is essential in order to reduce the environmental and health risks associated with the use of waste water.

The main objective of this thesis was to compare the concentrations and distributions of metals within waste water irrigated systems in Bang B village, Thanh Tri district, a peri-urban area downstream Hanoi City, Vietnam. The reverse aqua regia extractable (AqReg) and exchangeable (Exch) concentrations of Cu, Cd, Zn and Pb in soil and surface sediment were quantified within two irrigation systems along preselected distance gradients from a concrete irrigation canal. In a "from earth-canal to field" irrigation system, the pumped waste water flowed from an earth canal to the connected fields through openings along the side of the canal. In a "from field to field" irrigation system, the pumped water flowed from one field to another through openings in the earth walls surrounding each field.

Within water flow gradients there were no statistically significant differences in soil metal concentrations, which were associated with the distance from the concrete irrigation canal. However, there were significant differences within the sampled soil profiles, the values being higher in surface layers than in deeper layers. These results indicate an accumulation of trace metals in the soil due to anthropogenic sources, such as the waste water used for irrigation. In all soil and sediment samples the AqReg metal concentrations were below the international maximum permissible levels. AqReg metal concentrations (per kg dry soil) ranged from 15 to 27 mg Cu kg^{-1}, 55 to 93 mg Zn kg^{-1}, 0.1 to 0.4 mg Cd kg^{-1} and 13 to 32 mg Pb kg^{-1}. The Exch metal concentrations in soil and sediment samples were generally low, which meant a similarly low Exch metal/AqReg metal ratio. Exchangeable metal concentrations (per kg dry soil) ranged from below the detection limit to 0.2 mg Cu kg^{-1}, 0.008 to 0.9 mg Zn kg^{-1}, 0.0003 to 0.03 mg Cd kg^{-1} and from below the detection limit to 0.02 mg Pb kg^{-1}. Other studies of waste water irrigation in Vietnam and in other similar countries, reported higher concentrations of metals accumulated in soil. The low concentrations found in Hanoi could probably be explained by the early stage of industrial development in this city.

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1 Introduction

1.1 Waste water for irrigation

1.1.1 Untreated waste water around the globe

Many cities in developing countries face problems in connection with food security for their growing populations. There may also be associated problems concerning the supply of clean drinking water and the management of solid and liquid wastes. Two thirds of the waste water produced world-wide receives no treatment at all (Raschid-Sally *et al*., 2001). If untreated waste water is discharged into rivers and lakes, there is a danger of pollution to surface and ground water sources of drinking water. Discharged waste water may facilitate the transmission of disease-causing microorganisms and cause other serious effects such as fish kills (Alhumoud *et al*., 2003).

It is generally agreed that waste water should receive some treatment in order to decrease the concentrations of various toxic elements and thus reduce the environmental risks associated with those elements. However, still many national governments lack economic and political means to build water treatment plants or enforce regulations (IWMI Research update, 2004). The cost of installing sewer systems is at least as high as the cost of building treatment facilities. In addition, the operation and maintenance expenses associated with sewers are very high. Cities standing on river deltas or situated in coastal areas with small topographical gradients face problems associated with inadequate operation and maintenance of the sewer network. This may lead to sewer clogging, local flooding, and pipe leakage resulting in soil and groundwater pollution (Nguyen Viet Anh, 2002).

1.1.2 Waste water in agriculture

Irrigation of arable land represents a significant fraction of the total demand for fresh water. Waste water used for irrigation is essential in many countries. Worldwide, it is estimated that 20 million hectares of arable land are irrigated with waste water. Studies in several Asian and African cities suggest that agriculture based on waste water irrigation accounts for 50 percent of the vegetable supply to urban areas. Waste water reuse in agriculture is an alternative to treatments aimed at achieving the strict standards for waste water disposal into watercourses. Waste water irrigation saves freshwater which is particularly important in areas suffering from water shortage (Alhumoud *et al*., 2003). Farmers generally do not consider environmental benefits or hazards and are foremost interested in maximizing their yields and profits (Haruvy *et al*., 1999). Waste water is a valuable resource. It allows low-income farmers to produce crops they otherwise would not afford to grow. It is also a reliable resource of water, even during dry seasons and contains valuable nutrients for the crops. The high nutrient content may improve the yield and lead to significant savings on costly mineral fertilizers. However, there are health risks to consider both for farmers and consumers. Direct contact with the untreated waste water exposes farmers to pathogenic viruses and bacteria, as well as toxic elements. Bacteria and toxic elements can also be transmitted to crops which in their turn might harm consumers (IWMI Research update, 2004). Since several trace metals are toxic even at rather low concentrations, their accumulation in agricultural soils may affect the microbial activity as well as plant growth and plant quality (Alloway, 1995; Langley *et al*., 2003).

1.1.3 Complex waste water in Hanoi

In 2004 Vietnam had a population of 81.5 million people (Nationalencyklopedin, 2005), of which approximately 23 percent lived in urban areas, and about 30 cities used waste water for irrigation. (Nguyen Viet Anh, 2002). The country is undergoing a rapid industrialization and urbanization. Hanoi, the capital and second largest city, has experienced a rapid economical development and urbanisation more or less without city planning which has caused various

environmental problems. The city has neither a piped sewage system nor any water treatment plant. Domestic, industrial, and hospital waste water is collected in open street drains before being discharged into the rivers, which have become waste water collectors. The street drains have gradually become enclosed channels in order to improve the sanitary conditions in the streets (Ho Thi Lam Tra *et al*., 1998; Ho Thi Lam Tra and Egashira, 2000).

The mixing of all kinds of waste water leads to a highly complex solution which contains many pollutants, which vary both in their composition and concentration. Consequently effective removal of pollutants has become very difficult (Ho Thi Lam Tra *et al*., 2000; Chilton and Kinniburgh, 2002; Nguyen Viet Anh, 2002).

1.1.4 Accumulation in soils

As a result of the use of waste water for irrigation, trace metals have accumulated in agricultural soils (Flores *et al*., 1997; Ho Thi Lam Tra *et al*., 1998; Ho Thi Lam Tra and Egashira, 1999; Chilton and Kinniburgh, 2002; Jiries *et al*., 2002; Nguyen Ngoc Quynh and Le Huy Ba, 2002; Lucho-Constantino *et al*., 2004).

The connection between soil and water contamination and metal uptake by plants is determined by many chemical and physical soil factors as well as the physiological properties of the crops. Soils contaminated with trace metals may pose both direct and indirect threats: Direct, through negative effects of metals on crop growth and yield, and indirect, by entering the human food chain with a potentially negative impact on human health. Even a reduction of crop yield by a few percent could lead to a significant long-term loss in production and income. Some food importers are now specifying acceptable maximum contents of metals in food, which might limit the possibility for the farmers to export their contaminated crops. Therefore the protection of soils from trace metal pollution is essential for maintaining a good soil and food quality. Once contaminated, it is difficult and expensive to decontaminate soils (Chilton and Kinniburgh, 2002).

1.2 Trace metal concentrations in agricultural soils

The total metal content (M_{tot}) in the soil is the sum of all inputs and outputs. Input sources are weathering of parent material (M_p), atmospheric deposition (M_{ad}), fertilizers (M_f), pesticides (M_{pe}), organic wastes (M_{ow}) and inorganic pollutants (M_{ip}). Outputs are removal of crops (M_{cr}), leaching (M_l) and volatilisation (M_v). The main input and output source of metals in this study is probably waste water (in) and crop off-take (out), respectively.The total metal content in the soil can thus be expressed by the following equation: $M_{tot} = (M_p + M_{ad} + M_f + M_{pe} + M_{ow} + M_{ip}) – (M_{cr} + M_l + M_v)$. The equation covers the total concentration of metals while metal speciation, i.e. identification of bioavailable metal fractions is a more complex issue (McBride, 1994).

1.2.1 The soil-plant system

The following factors affect metal uptake by plants: (1) the concentration and chemical speciation of the metals in the soil solution, (2) the movement of the metal from the bulk soil to the root by diffusion or convection, (3) metal absorption by the root and (4) metal translocation within the plant. The plant uptake of mobile ions present in the soil solution is determined by a combination of the total quantity of that specific ion in the soil and other soil factors such as pH, EC (Electrical Conductivity) and organic matter content. Absorption of metals by plant roots can be both passive and active. Passive uptake involves diffusion of ions in the soil solution into the root endodermis along a chemical potential (appr. concentration) gradient. Active uptake takes place against the concentration gradient and therefore requires metabolic energy. The type of uptake varies among different metals. Lead (Pb) uptake is generally

considered to be passive while uptake of copper (Cu) and zinc (Zn) is thought to be either active, or a combination of active and passive. Absorption mechanisms can vary between different metals. Metal ions that are absorbed by the same mechanism are likely to compete with each other. Cadmium (Cd) and Zn have high transfer coefficients (expressed as total metal concentration taken up in aboveground biomass divided by total metal concentration in soil). Cadmium and Zn are thus easily taken up and translocated through the xylem vessels to the plant tops. Copper is intermediate and Pb is translocated to the least extent (Alloway, 1995).

1.2.2 Trace metal toxicity

Excessive concentrations of both essential and non-essential metals in plants may result in phytotoxicity. The toxic effect of a metal is determined more by its chemical speciation than by its concentration (Langley et al., 2003). Human exposure to toxic concentration levels of metals may have negative effects on individual organs in the body and cause either direct poisoning or various diseases (Baldwin and Marshall, 1999). Copper and Zn are two important essential elements for plants, microorganisms, animals and humans. Cadmium on the other hand has no essential biological function and is generally toxic. The major threat to human health is chronic accumulation in the kidneys leading to kidney dysfunction. Food intake and tobacco smoking are the main routes by which Cd enters the body. Lead is not an essential element, either. It is well known to be toxic and its effects have been more extensively reviewed than the effects of other trace metals. Lead can cause serious injury to the brain, nervous system, red blood cells and kidneys (Baldwin and Marshall, 1999).

1.3 Availability of metals

High total concentrations of metals in the soil can either indicate high background concentrations in the geological parent material, or pollution from human activity. However, a measure more useful than total element concentration is an estimate of the bioavailability. In this way the metal concentration can be related to plant uptake, mobility, and chemical extractability. Some metals are at least partially extractable with solvents such as water or diluted salt solutions, while others might resist extraction by chemically aggressive solutions such as strong acids or powerful chelating agents. Neither the total quantity in the soil nor the quantities extracted by aggressive reagents are closely related to the plant availability of the element. The concentration in the soil solution often seems to be a better measure of availability. But still the soil solution concentration explains only a part of the complex equilibrium (McBride, 1994).

The most important chemical processes affecting the behaviour and bioavailability of metals in soils are those concerned with the adsorption of metals in the solution on solid soil surfaces. Adsorption processes control the free ions and ion complexes in the soil solution and thus exert a major influence on metal uptake by plants. Several different mechanisms can be involved in the adsorption of metal ions, including (1) cation exchange (non-specific adsorption), (2) specific adsorption, (3) co-precipitation and (4) organic complexation. It is difficult to specify which particular process that is responsible for the retention of metals in any particular soil (Alloway, 1995).

1.3.1 Cation exchange

Most trace metals exist mainly as cations in the soil solution and their adsorption therefore depends on the density of negative charge on the surfaces of soil colloids. Cation exchange is reversible and in most cases there is a selectivity or preference for one ion compared to another. This selectivity gives rise to a replacing order among the cations. The higher the charge of an ion, the greater is its replacing power (McBride, 1994; Alloway, 1995).

1.3.2 Specific adsorption

Specific adsorption involves the exchange of trace metal cations and many anions with surface ligands, to form partly covalent bonds with lattice ions. This results in a higher degree of metal adsorption than expected from the CEC (cation exchange capacity) of the soil. Specific adsorption is related to the hydrolysis of the trace metal ions. The metals most likely to form hydroxyl complexes are specifically adsorbed to the greatest extent (Alloway, 1995).

1.3.3 Co-precipitation

Co-precipitation is defined as the simultaneous precipitation of a chemical agent in conjunction with other elements by any mechanism and at any rate. The types of mixed solids commonly formed include clay minerals, hydrous Fe and Mn oxides and calcite in which isomorphous substitution has occurred. Trace metals can form insoluble precipitates which could play a role in controlling their solubility in the soil solution (Alloway, 1995).

1.3.4 Complexes with organic matter

The chelating effect of solid humic substances contributes to the stability of metal-organic complexes. Low-molecular organic ligands, such as those of oxalic acid anions $(COO^-)_2$, can form soluble complexes with metals and thereby prevent them from being adsorbed or precipitated (Alloway, 1995). The complexes mentioned, involve some covalency, and the strength of the bond is sensitive to the chemical properties of the metal as well as the organic coordinating groups. The negatively charged surface of the organic matter also functions as a cation exchanger with non-selective electrostatic forces. For this type of adsorption, the charge and hydrated radius of the metal ions are the most critical factors controlling selectivity. Some surface complexes are very strong however, and resist dissociation over a very wide pH range. Potential cation sites on organic matter are therefore blocked by the complexed metals, reducing CEC (McBride, 1994). Humic matter contains hydroxyl, phenoxyl and carboxyl groups, which play a dominant role in metal binding (Alloway, 1995).

1.3.5 pH and cation exchange

For many metals, pH is a “master variable” controlling the degree of metal hydrolysis and metal precipitation. Trace metals occurring as cations are most soluble and mobile under acid conditions and thus more available to plants. Reducing conditions often cause a pH increase and a decrease in concentration of soluble metals. The soil colloids will get more negative charge when pH increases and therefore the capacity to adsorb trace metals will increase (McBride, 1994).

1.3.6 Speciation and availability

Bonding of metals with ligands in soil solution is important in determining the chemical behaviour and toxicity of metals. A large fraction of the metal ions in soil solution may be complexed with either organic or inorganic ligands. For instance Cd forms complexes with Cl^- ions. Organic ligands significantly increase the carrying capacity of the soil solution for strongly complexed metals like Cu^{2+}, thereby increasing total metal solubility. pH-dependent ligands like OH^-, HCO_3^-, CO_3^{2-} and organic anions increase in concentration as pH increases. At the same time metal cation adsorption at mineral and organic surfaces is favoured. Therefore, total metal solubility in soil solutions often shows a two-stage trend, decreasing up to pH 6 or 7, but increasing again at higher pH as soluble ligands gain in importance and bring the metals into solution. The Cu^{2+} ion for instance, forms stable complexes with OH^-, HCO_3^- or functional groups on organic matter. Soluble organic matter often acts as a cation carrier. When the roots take up Cu^{2+} ions for instance, the soluble complexes supply copper at the root surface at a much faster rate than the diffusion of free Cu^{2+} ions. Soils that are high in clay minerals, oxides, or humic compounds strongly retain most of the trace metals (McBride, 1994).

1.3.7 Copper availability

Copper in soil commonly occurs as the divalent cation Cu^{2+}. Under most conditions copper is found in the adsorbed (soil-Cu) form, which is usually more stable than any Cu minerals (Alloway, 1995). Reduction of Cu^{2+} to Cu^{+} and Cu^{0} is possible under reducing conditions. In reduced soils copper has a very low mobility. Most of the colloidal material of soils (oxides of Mn, Al, Fe, silicate clays and humic substances) adsorb Cu^{2+} strongly, and increasingly when pH is raised. Copper is a low mobility metal in near-neutral soils. In more alkaline soils, soluble complexes of Cu^{2+} can form and increase the total copper solubility (McBride, 1994).

1.3.8 Zinc availability

In acid aerobic soils Zn has a medium mobility and it is one of the most soluble trace metals. In neutral soils the mobility is very low due to chemisorption (i.e. specific adsorption) on oxides and aluminosilicates as well as complexation with humic matter. In alkaline soils the free Zn^{2+} ion concentration is very low but Zn^{2+}-organic complexes may become soluble and raise the Zn solubility. Under reduced conditions the mobility is very low due to the very low solubility of ZnS (McBride, 1994).

1.3.9 Cadmium availability

The Cd^{2+} ion adsorbs rather weakly on organic matter, silicate clays and oxides unless pH is greater than 6. Above pH 7 Cd^{2+} can co-precipitate with $CaCO_3$ or precipitate as pure $CdCO_3$, and Cd phosphates may limit the solubility as well. As a result, mobility and bioavailability of Cd in neutral to alkaline soils are low (McBride, 1994), and octavite ($CdCO_3$) could be a major factor controlling Cd solubility in high pH soils. In flooded paddy soils with reducing conditions CdS can be formed, which can explain the low solubility of Cd in these soils (Alloway, 1995).

1.3.10 Lead availability

Lead exists principally in the Pb^{2+} form in solid soil material and soil solution. Lead is almost insoluble in reduced soils. Under oxidizing conditions Pb^{2+} becomes less soluble as pH increases. Complexation with organic matter, chemisorption on oxides and silicate clays, and precipitation as carbonate, hydroxide, or phosphate are all favoured at high pH. In alkaline soils the solubility may increase due to formation of soluble Pb^{2+}-organic and Pb^{2+}-hydroxy complexes. Lead is the least mobile trace metal in soils, especially under reducing or non-acid conditions (McBride, 1994).

1.4 Project description

The fieldwork of this thesis was carried out during a three-month period from 3 September to 25 November 2004. It was a Minor Field Study (MFS), associated with the project 'Sustainable Farming at the Rural-Urban Interface –An Integrated Knowledge Based Approach for Nutrient and Water Recycling in Small-Scale Farming Systems in Peri-Urban areas of China and Vietnam' (RURBIFARM). The project was funded by the European Union (EU) for a four-year period, 2002-2006 (ICA4-CT-2002-10021). It was a joint project with the following research partners:

(1) The Swedish University of Agricultural Sciences (SLU)
(2) The Institute of Soil Science, Chinese Academy of Sciences (ISSAS), Nanjing, China
(3) The National Institute for Soils and Fertilizers (NISF), Hanoi, Vietnam
(4) The Vietnam Environment and Sustainable Development Institute (VESDI), Hanoi, Vietnam
(5) The University of Wales, Bangor (UWB), UK
(6) The Multiple Cropping Centre of Chiangmai University (CMU) Thailand
(7) The World Agroforestry Centre (ICRAF) in SE Asia.

The activities described in this thesis belonged to the Rurbifarm work package 4, the objective of which was 'to evaluate the environmental impacts by current farming systems concerning the use of urban wastes, pesticides, and fertilizers in a short and long-term perspective and in a field and catchment scale' (RURBIFARM, 2002).

2 Hypotheses and objectives

The following hypotheses were tested in this thesis:

- Trace metals are to a great extent transported in water associated with organic matter. Therefore, 'Chemical Oxygen Demand' (COD) and total suspended solids could be two qualitative indicators of concentrations and distributions of trace metals in water covering the soil surface of vegetable fields during water pumping.
- Trace metal concentrations in waste water will decrease with distance from the pumping source due to sedimentation. This phenomenon will be reflected by the spatial metal concentration gradients in soil and surface sediment.
- The trace metal concentrations in soil and surface sediment in the irrigation systems, "earth-canal to field" and "from field to field" will differ due to differences in irrigation water pathways and flow velocities (see 3.2.3 Selected gradients).

The specific objectives of this thesis were to:

- Determine the aqua regia extractable and exchangeable concentrations of Cu, Zn, Cd and Pb in soil and sediment along selected gradients and at various soil depths within two irrigation systems.
- Measure the variation in COD and total suspended solids in water in the two irrigation systems at different time intervals during the pumping of waste water.
- Cross-check obtained research data with previously collected Rurbifarm monitoring data, particularly from work package 3 of the Rurbifarm project: 'Element balances and crop quality. Risk assessment'.
- Explore relationships between trace metal concentrations in soil, sediment and crops (vegetables). The trace metal concentrations of the vegetables were provided by the Rurbifarm work package 3.

3 Materials and methods

3.1 Site description

3.1.1 Climate and soils

Hanoi has a tropical monsoon climate with two main seasons. The dry season, which lasts from October to April, is cool with little rainfall. The wet season, which lasts from May to September is hot with heavy rains. During the year of study, the annual mean temperature was 26.5ºC, and the annual rainfall was 1243 mm (Martin Larsson, personal communication).

The investigated soil is classified as a Eutric Fluvisol in the *FAO-UNESCO-WRB* classification system and as an Udifluvent in the *USDA* Soil Taxonomy system (NISF, 2003; Tra and Egashira, 1999). Fluvisols are young soils in *alluvial deposits* and occur in fluvial, lacustrine as well as marine deposits. Most Fluvisols are wet in all or part of the profile due to stagnating groundwater and/or flooding from rivers or tides. Most Fluvisols have a neutral or near neutral pH value which favours the availability of most nutrients. The good inherent fertility of most Fluvisols makes them suitable for paddy rice and vegetable cultivation. Thionic Fluvisols are the drastic exception, where pyrite (FeS_2) can be formed under reducing conditions, if iron and sulphur (seawater and brackish water contain sulphur) are present. The pyrite can be oxidized to sulphuric acid (H_2SO_4) if the pyritic sediment dries out, often causing severe acid

conditions. Paddy land should be kept dry for at least a few weeks every year to prevent the redox potential of the soil from becoming so low that nutritional problems (Fe^{2+} toxicity, formation of poisonous H_2S) arise.

The soil texture at the study site (see below) was silty loam in the top soil (0-15cm) layer, clay loam from 15 cm down to 60 cm, sandy loam between 76 cm and 112 cm, and sand below 112 cm. Roots were found down to a depth of 30 cm (NISF, 2003).

3.1.2 Bang B village

The Bang B village was selected as one of two villages to be included in the Rurbifarm project, for research on rural-urban interactions through the use of urban solid waste or waste water in agriculture (Hoang Fagerström *et al.,* 2006). The village belongs to Hoang Liet commune in the Thanh Tri district and is a typical peri-urban area. It is located 10 kilometres south of the central part of Hanoi city, close to the To Lich River. The total area of Bang B village is 48.6 hectares, of which 3.1 hectares are used for settlements, 28 hectares for rice fields, 11.3 hectares for vegetable and cereal fields, 2 hectares for fish ponds, and 4 hectares for other land use. The population of Bang B village is approximately 1400 people, and there are 368 households of which 303 are supported by agriculture. The local goal is to improve the livelihood of villagers in general and farmers in particular and to ensure the social security and political stability by increasing agricultural production of rice and vegetables which are the dominant crops (farming systems) in the village (RURBIFARM, 2003).

3.1.3 To Lich River

The To Lich River is 13 km long and flows from West Lake in the central part of Hanoi into the Nhue River. Nhue River connects with the Red River that finally reaches the South China Sea. On its way through Hanoi City, the To Lich River receives untreated domestic, industrial and hospital waste-water. The river has become a black and stinky waste-water drainage canal, and its water quality is extraordinarily bad. The contents of bacteria, nutrients, toxic chemicals and trace metals are high (Ho Thi Lam Tra *et al*., 1998; Rurbifarm, 2002). The water from the river is pumped into the fields of Bang B village for irrigation.

3.2 Research process

3.2.1 Criteria for soil, sediment and water sampling

It was important to find transects for soil, sediment and water sampling that received water from only one direction. The aim of the sampling was to explore relationships between metal concentrations and distance from the pumping source. Therefore, any influence from multiple flow pathways had to be avoided. In order to characterize the variation in COD and suspended solids along the chosen flow gradients it was necessary to know in advance at what time the pumping was to take place and to which fields the irrigation water was to be directed. A good personal contact with someone responsible for the pumping schedule was essential for the sampling to proceed as planned. Another important aspect was to include the two Rurbifarm fields BB1 and BB2 (Fig. 2), which had already been characterized and were included in a study of plant nutrient and trace metal balances. Element balances as well as crop quality in these two fields were investigated by NISF. In that way secondary data of the Rurbifarm project could be used as complementary information as well as for cross-checking of new results. Another aim was to find gradients representing the two water pathways resulting either from irrigation “from earth canal to field” or “from field to field”. A comparison of the pathways was important for the evaluation of the present way in which the waste water irrigation was handled. Finally, to be certain that the environmental conditions were as similar as possible regarding both quantities and pathways of irrigation water as well as biological and

chemical soil processes, all fields had to be used for growing aquatic vegetables, which meant that the fields should be saturated with water during most of the cropping season.

3.2.2 Water flow pathways

Water flow pathways to and between the fields were identified by visual observations in a three-step process. (1) Concrete- and earth-canals were identified to get a general picture of the irrigation system in Bang B village, (2) outlets from the concrete- and earth-canals, as well as inlets/outlets between the fields, were identified to find the possible pathways and directions of the waste water and (3) observations were made during pumping to verify the suggested water flows.

3.2.3 Selected gradients

There were many outlets along the concrete canals, which created a complex water flow pattern. In addition there were many earth canals, plus inlets/outlets between the fields, which increased the complexity even more. The directions and pathways of the flow to and between the fields could be changed by the farmer, depending on which field that needed water. In the "from earth-canal to field" irrigation the pumped water flowed from an earth canal to connected fields through openings along the side of the canal. In the "from field to field" irrigation the pumped water flowed from one field to the next through openings in the earth walls surrounding each field. The schematic map of Bang B village in Fig. 1 shows the directions of the irrigation water. The map does not show the many sub-fields, earth canals and inlets/outlets from the concrete canals to the earth canals and between the fields. According to the local farmers the location of the fields in the selected gradients had been unchanged since 1994.

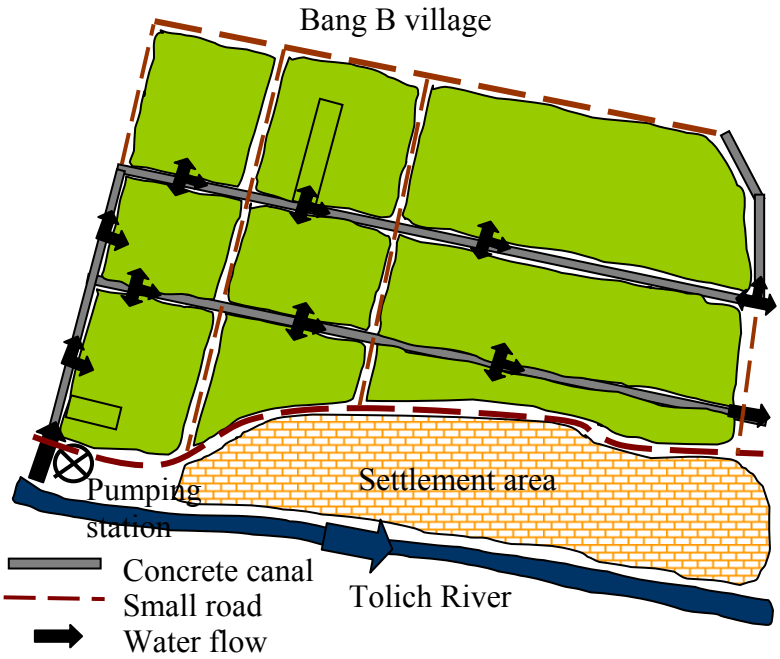

Fig. 1. Schematic map showing the water flow pathways in concrete canals in the Bang B village. The two rectangles delimited by thin black lines show the location of the fields included in the selected soil and sediment gradients.

Based on the criteria for soil, sediment and water sampling, two gradients for soil sampling, soil gradients 1 and 2 (SG1 and SG2), and four gradients for sediment sampling, sediment gradients 1, 2, 3 and 4 (SeG1, SeG2, SeG3 and SeG4) were chosen (Fig. 2). The idea was to collect water samples along the gradients used for soil and sediment sampling. However, it was difficult to get information about the pumping time in advance which made it difficult to collect a sufficient amount of water samples within the chosen gradients.

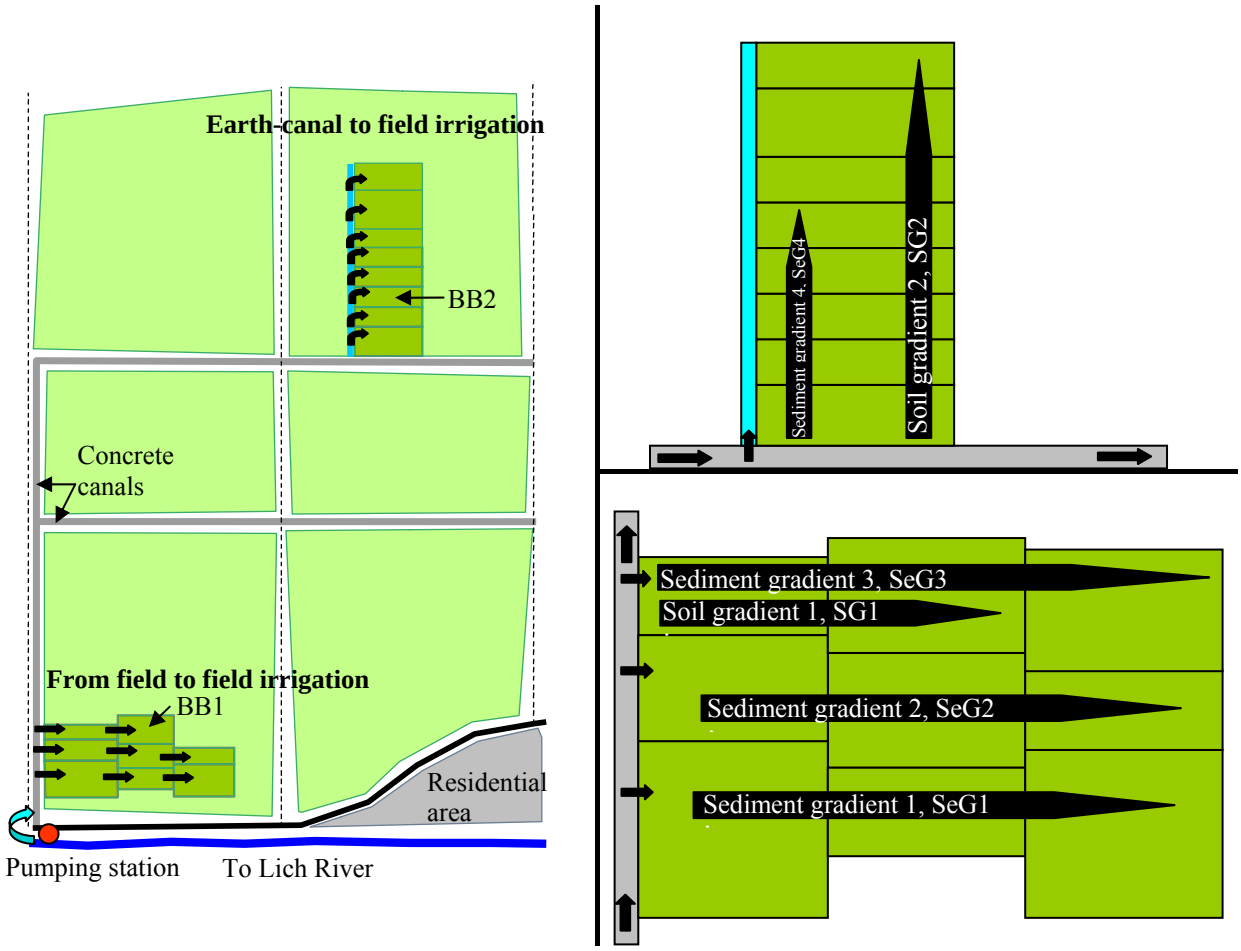

Fig. 2. Selected gradients for soil and sediment sampling in Bang B village. SeG 1-3 include three fields each, SeG 4 includes five fields. SG 1 and 2 consist of two and eight fields respectively.

3.3 Field sampling

3.3.1 Soil sampling

Soil samples were randomly collected within the selected fields using an auger. To avoid contamination of soil samples from water standing above the soil surface, an open plastic cylinder was placed on top of the soil surface on fields that were water saturated. The water inside the cylinder was removed by pumping to expose the soil surface to the open air. Thereafter a soil core was collected inside the cylinder. Each core was divided into four different layers, 0-15cm, 15-30cm, 30-60cm and 60-90cm. The samples were transferred to labelled plastic bags, and all sampling sites were marked on a map. In each field eight sub-samples were taken from the two upper layers, and four sub-samples from the two lower ones. To make one composite sample, all sub-samples originating from the same field and soil depth were mixed and put in a new plastic bag.

The criteria for selecting the soil depths 0-15cm, 15-30cm, 30-60cm and 60-90 cm were as follows:
1. The tillage depth in the fields varied between 10 and 20 cm which made the top 15 cm suitable for a representative sampling of that depth.
2. In the soil classification made by NISF (NISF, 2003), the soil horizons A_p (0-15), A_w (15-30), and B (30-60) were distinguished. Using the same sampling depths made the cross checking of analytical data much easier.

3. The effects of waste water irrigation could be tracked by taking samples at a greater depth (60-90cm), and then compare the metal concentrations at that depth with those of the shallow soil, which were supposed to be more affected by the waste water.

3.3.2 Sediment sampling

Five sediment sub-samples were randomly taken in each field and mixed into one composite sample. The top 1-2 cm surface layer was collected with a strainer and the samples were put in labelled plastic bags.

3.3.3 Water sampling

Water samples were planned to be taken along the selected gradients before pumping and at different time intervals after pumping. At each sampling point, water was collected in plastic bottles. Not more than 14 water samples could be collected each day due to logistical limitations.

3.4 Sample treatment

3.4.1 Soil sample treatment

The composite soil samples were air-dried at room temperature (about 25°C) in open plastic bags. Then the soil was crushed in a mortar and sieved through a 2 mm mesh prior to analysis. 200 g of each sample were transported to Sweden for EC, pH, water content, total organic carbon, total nitrogen and trace metal analyses.

3.4.2 Sediment sample treatment

The composite sediment samples were oven dried at 40°C in open plastic bags, the sediment was crushed in a mortar and sieved through a 2 mm mesh prior to analysis. 100 g of each sample were transported to Sweden for EC, pH, water content, total organic carbon, total nitrogen and trace metal analyses.

3.4.3 Water sample treatment

pH, EC, COD and total suspended solids were analysed on the day of sampling at the Environmental Technology Department, Hanoi University of Science.

3.5 Laboratory methods

3.5.1 Soil and sediment analyses

3.5.1.1 EC and pH

5 ± 0.01 g aliquots of air dry soil were weighed into plastic containers for pH measurements. 25 ml of aerated distilled water was added and the containers were closed with screw caps. The samples were shaken for one hour and allowed to settle for 20 minutes. EC was measured on the same samples before the pH measurements, in order to avoid salt contamination. The EC meter was calibrated with KCl standard solutions. The pH meter was calibrated with pH 4.01 and pH 6.86 buffer solutions before the pH readings. For pH measurements in 0.01 M $CaCl_2$, 0.5 ml 0.5 M $CaCl_2$ was added to the samples. The soil-salt solution suspensions were thereafter shaken for 30 seconds. The suspensions were allowed to settle for 20 minutes before the pH readings (Stevens, 2003).

3.5.1.2 Water content

5 g aliquots of air dry soil were weighed into pre-weighed porcelain crucibles. The samples were oven dried at 105°C for twelve hours and cooled in a desiccator before they were

weighed again. The weight loss was used for calculating the soil water content. (Laborationskompendium i marklära, 2001)

3.5.1.3 Total organic carbon (C) and nitrogen (N)

5 g aliquots of air dry soil were weighed into porcelain crucibles. 5 ml of 5 M HCl was added to the samples to remove carbonates. After 4 hours the samples were put in an oven that was set at 60°C and the samples were dried for 16 hours. The samples were thereafter ground in a ball mill and 2 mg aliquots were weighed into tin cups and analysed at 1050°C with an elemental analyzer (LECO CHN 932), using an infra-red and an electrical conductance detector for C and N content, respectively (Ahlström, 2001).

3.5.1.4 NH_4NO_3 extractable metals

10 g of air dry soil was weighed into 50 ml screw-capped centrifuge tubes. 25 ml of 1 M NH_4NO_3 was added and the tubes were shaken on an end-over-end shaker for two hours (Stevens, 2003). The samples were centrifuged at 3000 rpm for 20 minutes to allow the soil particles to settle. The extracts were filtered through OOH filters and diluted with 1 per cent concentrated HNO_3 (based on volume). The extracts were analyzed with an ELAN 6100 DRC (dynamic reaction cell inductively coupled plasma)- mass spectrometer (ICP-MS).

3.5.1.5 Reverse aquaregia (AqReg)

0.5 g of air dry soil was weighed into restricted neck digest tubes. 4 ml of concentrated HNO_3 and 1.5 ml of concentrated HCl were added to the tubes, which were left overnight (Stevens, 2003). On the next morning a heating block timer was set and the samples were heated at 75°C for 30 minutes followed by 100°C for 30 minutes, 110°C for one hour and finally 140°C for 5 hours. The samples were cooled to room temperature and diluted to a total volume of 50 ml with 1 % HNO_3. The solutions were filtered through OOH filters and analyzed with ICP-MS.

3.5.2 Water analyses

3.5.2.1 pH

pH was measured with a pH meter which was calibrated against the only available standard buffer solution of pH 4. Between every measurement the electrode was washed with distilled water (Eaton *et al*., 1995).

3.5.2.2 EC

The electrical conductivity of the water samples was measured using a conductivity meter (Eutech instruments CON 5), calibrated with standard Eutech instruments KCl solutions at 1.413 mS m^{-1}, 4.02 mS m^{-1} and 12.88 mS m^{-1}.

3.5.2.3 COD

COD is used as a measure of the oxygen equivalent fraction of dissolved organic matter that is susceptible to oxidation by a strong chemical oxidant. In samples collected at a specific site, COD can be empirically related to BOD (biological oxygen demand) or total dissolved organic C. COD is expressed as the corresponding concentration of oxygen that would be reduced and converted to H_2O (mg O_2 L^{-1}) (Eaton *et al*., 1995), and measurements can be used as a relatively quickly obtained indicator of the organic content in the water.

COD was analysed on the same day as the samples were collected, by using the closed reflux, titrimetric method. 2.5 ml of waste water sample, 1.5 ml of 0.0167 M standard potassium dichromate ($K_2Cr_2O_7$) digestion solution and 3.5 ml of sulphuric acid reagent (H_2SO_4) were mixed in culture tubes which were capped. For the blank, 2.5 ml of distilled water was used instead of waste water. The tubes were heated at 150 °C during two hours and thereafter cooled

until they reached room temperature (between 25 and 35ºC depending on the outdoor air temperature during the day of analysis). Five drops of Ferroin redox indicator were added to the samples. A magnetic stirrer was used, while the samples were titrated with a standard solution of ferrous ammonium sulphate titrant ($Fe(NH_4)_2(SO_4)_2$; abbr. FAS). The approximate initial concentration of Fe^{2+} was 0.1 M. The end point of the titration was defined by a sharp colour change from blue-green to reddish brown. The blanks were also titrated with FAS for calibration of the standard solution (Eaton, section 5220 C, 1995).

3.5.2.4 Total suspended solids dried at 103-105°C

Total suspended solids are defined as the portion of total solids that is retained by a filter, and total dissolved solids make up the portion passing through the filter. The type of filter holder, filter pore size, area, particle size and amount of material deposited on the filter are the main factors affecting the separation of suspended from dissolved solids (Eaton *et al*., 1995). 50 ml of waste water sample was filtered through a pre-weighed Munktell OH cellulose filter paper. The filter was then dried at 103 °C for one hour and cooled in a desiccator during the night. On the next day the filters were weighed again and the difference in weight was regarded as the total suspended solids in the waste water (Eaton, section 2540 D, 1995).

3.6 Quality assurance

In order to check the quality of the analyses the Kungsängen reference soil sample was included in the extraction and analyses scheme. The reverse aquaregia concentrations of Cu, Zn, Cd and Pb in the reference soil sample were compared with recent measurements of the same material (Table 1). The obtained average concentrations were just below recent mean values.

Table 1. Reverse aquaregia concentrations of Cu, Zn, Cd and Pb in the Kungsängen reference sample (Control) compared with recent measurements of the same reference material

Reverse aquaregia	Cu (mg kg^{-1})	Zn (mg kg^{-1})	Cd (mg kg^{-1})	Pb (mg kg^{-1})
Control 1	24.6	98.3	0.15	22.1
Control 2	25.0	98.3	0.15	21.7
Control 3	25.6	101	0.15	22.7
Control 4	25.4	100	0.14	22.3
average	25.1	99.4	0.15	22.2
040628	28.9	111	0.16	23.8
040628	29.2	107	0.16	22.4
040629	27.2	100	0.17	27.2
040629	28.8	111	0.15	22.5
041005	25.6	104	0.15	24.1
041005	25.6	104	0.17	23.4
041006	26.8	103	0.14	23.9
041006	26.5	102	0.13	22.8
average	27.3	105	0.15	23.8

To check if the samples were contaminated during the laboratory work, trace metal concentrations in the blanks were considered. The concentrations (ppb) of metals in the blanks used in the reverse aquaregia (Aq Reg) and NH_4NO_3 methods were compared with the minimum and maximum concentrations (ppb) of trace metals in the soil and sediment samples (Table 2). The detection limits for Cu, Zn, Cd and Pb were 0.4 ppb, 2.0 ppb, 0.04 ppb and 0.4 ppb, respectively.

Table 2. Blank values (ppb) in the reverse aqua regia and NH_4NO_3 extracts . The sample concentrations have been corrected for the average blank concentration. The Min and Max concentrations for the samples analysed have not been corrected.

Reverse aquaregia blank

ppb	Cu	Zn	Cd	Pb
Blank 1	0.36	5.28	<0.04	0.72
Blank 2	0.21	1.04	<0.04	5.80
Blank 3	0.23	2.27	<0.04	1.48
Blank 4	0.36	6.41	<0.04	0.82
Min sample	146	542	0.70	130
Max sample	280	1000	4.71	319

NH_4NO_3 exchangeable blank

ppb	Cu	Zn	Cd	Pb
Blank 1	2.71	<2.00	0.06	<0.40
Blank 2	2.76	*5.52*	<0.04	0.65
Blank 3	2.55	<2.00	<0.04	<0.40
Blank 4	2.61	<2.00	<0.04	<0.40
Min sample	0.53	3.48	0.12	<0.40
Max sample	82.1	350	3.68	4.34

The reverse aquaregia blanks had minimal concentrations compared to the samples, while the NH_4NO_3 blanks had high concentrations compared with the low exchangeable metal concentrations. Therefore some samples analysed for exchangeable metals got values below the detection limit after blank correction. The largest variability of the blanks was found for Zn and Pb. This trend was also observed in the next data verification test, where comparisons between duplicate samples demonstrated that Zn and Pb showed the largest variation in concentration. The reverse aquaregia and NH_4NO_3 extractable metal concentrations and ratios between the replicates are compared in Table 3.

Table 3. The reverse aquaregia and NH_4NO_3 extractable metal concentrations and ratios between the replicates

Reverse aquaregia	**Cu ($mgkg^{-1}$)**	**Zn ($mgkg^{-1}$)**	**Cd ($mgkg^{-1}$)**	**Pb ($mgkg^{-1}$)**
Sample no. 10	18.21	65.27	0.137	20.40
Duplicate	19.08	67.95	0.138	20.75
Ratio	1.048	1.041	1.008	1.017
Sample no. 20	14.78	54.65	0.083	12.86
duplicate	15.01	56.41	0.105	13.20
ratio	1.015	1.032	1.269	1.027
Sample no. 30	19.50	66.42	0.130	21.26
duplicate	19.05	66.46	0.118	19.59
ratio	0.977	1.001	0.912	0.921
Sample no. 40	16.58	58.55	0.093	15.34
duplicate	18.33	64.25	0.108	16.78
ratio	1.105	1.097	1.159	1.094
Sample no. 61	26.54	93.27	0.270	31.73
duplicate	27.91	96.53	0.283	33.22
ratio	1.052	1.035	1.048	1.047
NH_4NO_3 extractable				
	Cu	**Zn**	**Cd**	**Pb**
Sample no. 10	0.004	0.049	0.001	0.001
duplicate	0.005	0.043	0.001	0.001
ratio	1.250	0.872	1.000	1.000
Sample no. 20	<0.0004	0.029	0.003	0.001
duplicate	<0.0004	0.035	0.003	0.001
ratio	-	1.201	1.000	1.000
Sample no. 30	<0.0004	0.022	0.001	<0.0004
duplicate	0.001	0.057	<0.00004	<0.0004
ratio	-	2.591	-	-
Sample no. 40	<0.0004	0.016	0.001	<0.0004
duplicate	<0.0004	0.061	0.001	<0.0004
ratio	-	3.813	1.000	-
Sample no. 61	0.029	0.048	0.002	<0.0004
duplicate	0.028	0.053	0.002	<0.0004
ratio	0.966	1.104	1.000	-

The variations between the duplicates indicate some contamination during the laboratory process and/or variability in the analyses.

3.7 Methods for statistical analyses

3.7.1 Standard deviation and probability

In the statistical calculations metal concentrations of the sediment samples in SeG3 and SeG4 were assumed to be representative for the top layer in the soil gradients SG1 and SG2. The soil layers were thus 0-2cm, 0-15cm, 15-30cm, 30-60cm and 60-90cm. The calculated standard deviations are expressed in the same units as the observations (mg kg^{-1}) and show the absolute variation, which is scale dependent.

3.7.2 Bonferroni Simultaneous Tests

Multiple comparisons of mean values permit an examination of which mean values that are significantly different and an estimate of how much they differ. The Bonferroni multiple-comparison test was used to calculate if there were significant differences between soil layers. Pair-wise combinations of means of soil depths and fields were made. The Bonferroni method is a conservative method, which means that the true error is less than the estimated one (Johnson, 2000).

3.8 GIS and concentration distribution maps

To obtain a good overview of the horizontal and vertical distributions of AqReg and exchangeable trace metal concentrations as well as EC and pH values, maps of selected fields were made in the Global Information System (GIS) program Arc GIS 9. The maps show the concentrations along four sediment gradients SeG1, SeG2, SeG3 and SeG4, and in two soil layers (0-15 cm) and (60-90 cm) along the two soil gradients SG1 and SG2.

3.9 Crosschecking with NISF data

Soil and plant samples collected by the NISF staff were analyzed in their laboratory. Soil samples were digested with reverse aquaregia (volume ratio $1HNO_3$: 3 HCl) (Stevens, 2003). Plant samples were digested using a 5:1 nitric and perchloric acid mixture. Cu, Zn and Pb concentrations in soil samples and Cu and Zn in plant samples were determined by flame atomic absorption spectrophotometry (Perkin Elmer 3300), (RURBIFARM, 2004). The soil samples collected in the present study were analyzed at SLU as described above (see 3.5.1.5). Crosschecking of analyses between NISF and SLU were made on soil samples (0-15cm) from the two fields BB1 and BB2.

4 Results of soil and sediment analyses

The measured concentrations of Cu, Zn, Cd and Pb in soils and sediments in the present study were compared with international maximum permissible levels, to judge whether the Bang B values were high or acceptable compared to the standards launched in other countries (Table 4).

Table 4. Maximum permissible levels of total metal concentrations in mg kg^{-1} in arable soils in Vietnam (at different pH values), UK and Canada (Ho Thi Lam Tra et al., 1998). Also shown are Swedish maximum permissible levels for application of sewage sludge on arable soil (SNFS, 1998) and the total metal concentrations in soils and sediments found in the present study.

										Vietnam	**UK**	**Canada**	**Sweden** [a]	**Bang B**
pH	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0					
Cu	20	25	40	60	120	250	260	270	280	140	63	40	15-27	
Zn	30	40	60	90	200	320	340	360	370	280	200	100	55-93	
Cd	-	-	-	-	-	-	-	-	-	1-3	1.4	0.4	0.1-0.4	
Pb	25	30	40	50	70	80	80	80	80	35	70	40	13-32	

[a] The Swedish legislation includes the maximum permissible levels for sewage sludge application on arable soils and is not related to soil standards for agricultural use, hence these values have not been used in the evaluation of soil data from Bang B village.

For all trace metals, the concentrations at Bang B were below the Canadian and Vietnamese standards. Compared to the permissible international levels, all metal concentrations were within the set standards, except for Cd in two sediment samples.

The concentrations of AqReg and exchangeable trace metals were higher in the sediment and top soil layers, indicating metal accumulation due to for example waste water irrigation. The ranges of AqReg and exchangeable Cu, Zn, Cd and Pb in soils and sediments are shown in Table 5.

Table 5. Ranges of AqReg and exchangeable Cu, Zn, Cd and Pb concentrations in soil and sediment samples at Bang B.

Bang B village	**Cu**	**Zn**	**Cd**	**Pb**
Tot. conc. (mgkg^{-1})	14.78-26.89	54.65-93.48	0.070-0.449	12.86-31.73
Exch. conc. (mgkg^{-1})	<0.0004-0.202	0.008-0.870	<0.00004-0.029	<0.0004-0.017

The between-field distribution of metals was more complex than the vertical distribution within the soil profile. There were no obvious metal concentration gradients between the fields. However, some trends could still be indicated by inspecting the maps showing the concentration distributions.

4.1 Reverse Aqua Regia extractable (AqReg) metal concentrations

4.1.1 Distribution between the fields

AqReg concentrations of Cu, Zn, Cd and Pb in the sediment layer (0-2 cm) are shown in Figs. 3-6.

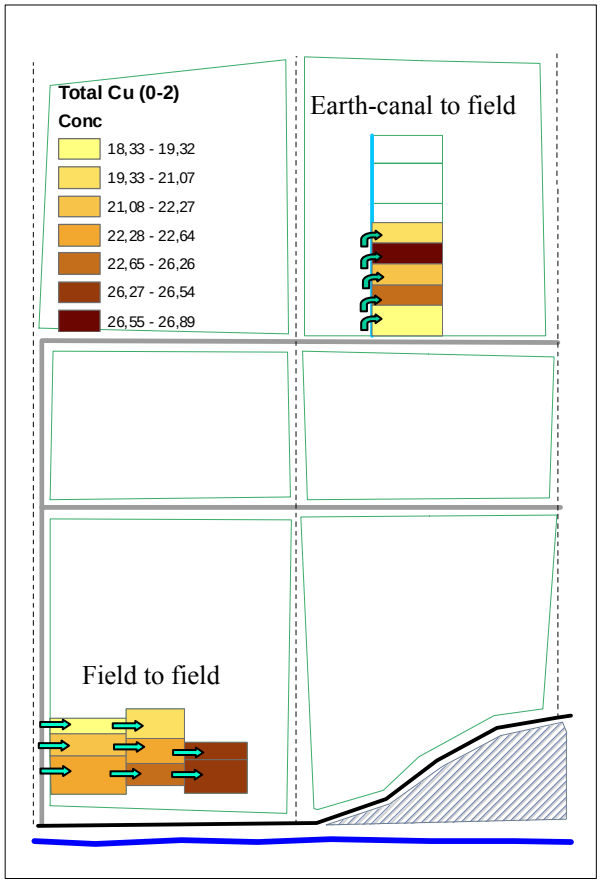

Fig. 3. Between-field distribution of AqReg Cu (mg kg^{-1}) in the sediment layer (0-2 cm)

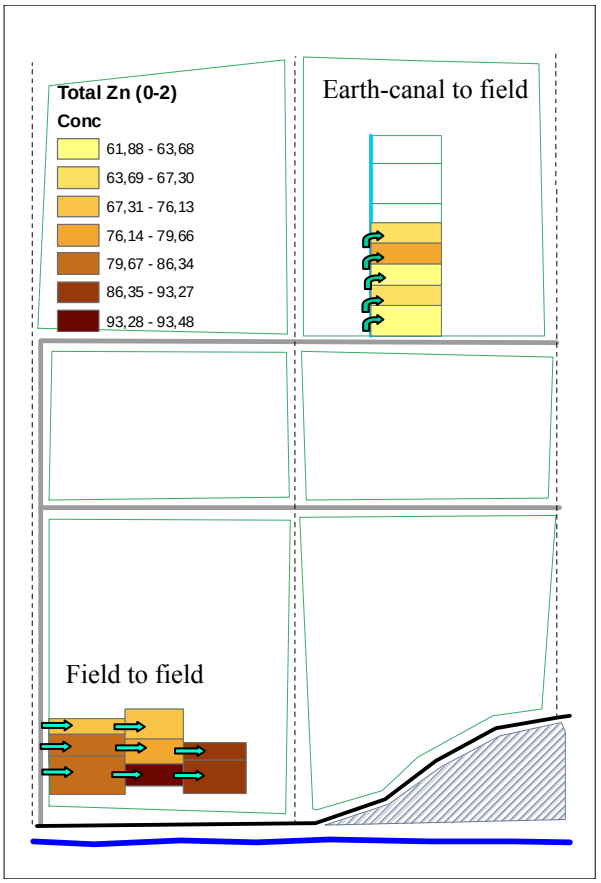

Fig. 4. Between-field distribution of AqReg Zn (mg kg^{-1}) in the sediment layer (0-2 cm)

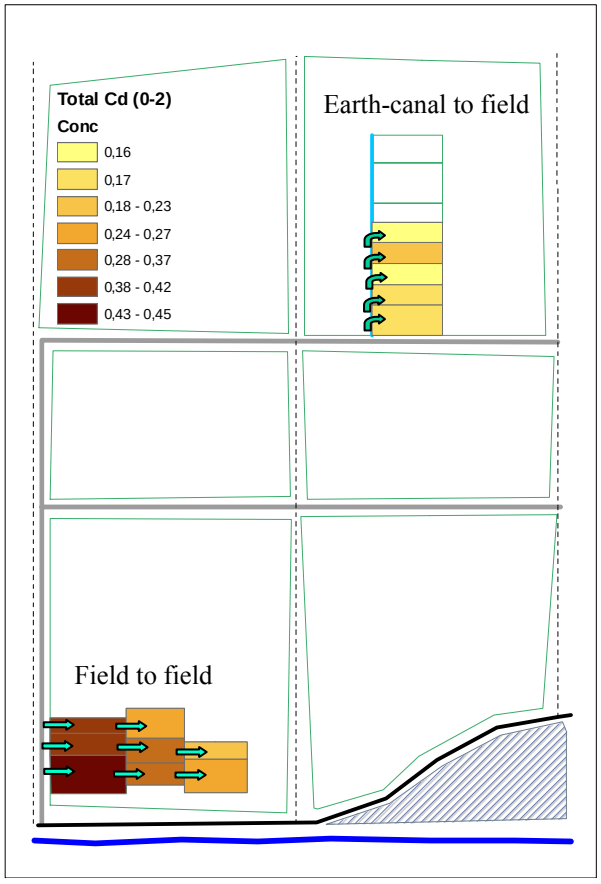

Fig. 5. Between-field distribution of AqReg Cd (mg kg^{-1}) in the sediment layer(0-2 cm)

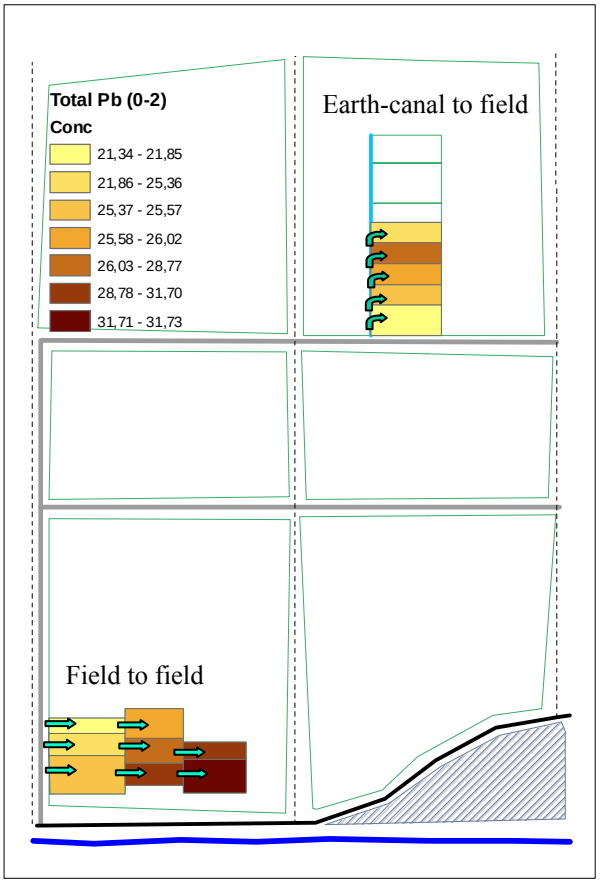

Fig. 6. Between-field distribution of AqReg Pb (mg kg^{-1}) in the sediment layer(0-2 cm)

AqReg concentrations in the 0-15cm soil layer are shown in Figs. 7-10.

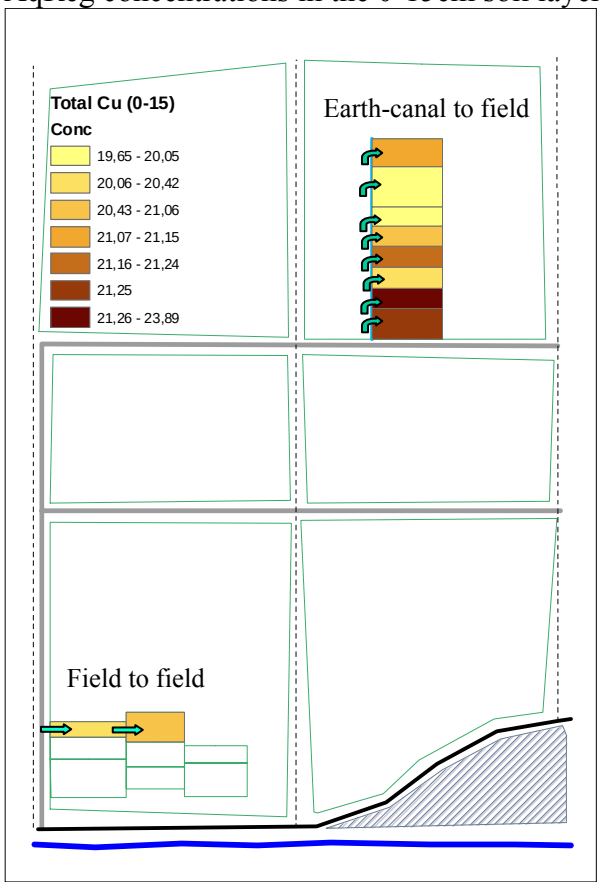

Fig. 7. Between-field distribution of AqReg Cu (mg kg^{-1}) in the 0-15 cm soil layer

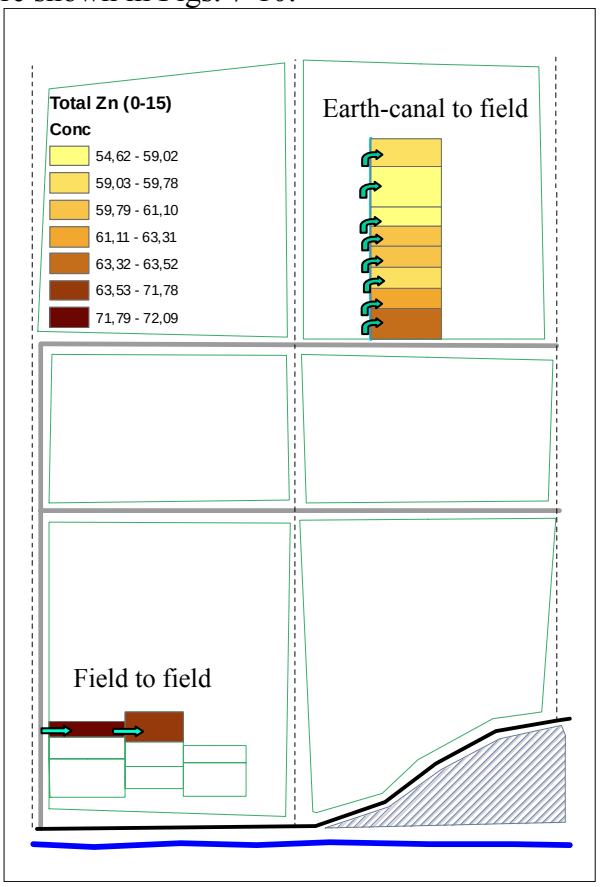

Fig. 8. Between-field distribution of AqReg Zn (mg kg^{-1}) in the 0-15 cm soil layer

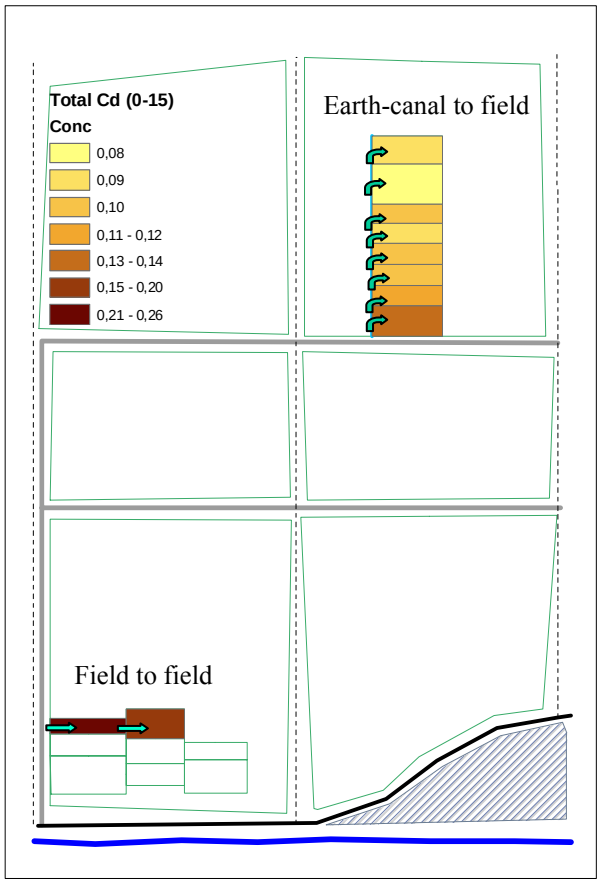

Fig. 9. Between-field distribution of AqReg Cd (mg kg^{-1}) in the 0-15 cm soil layer

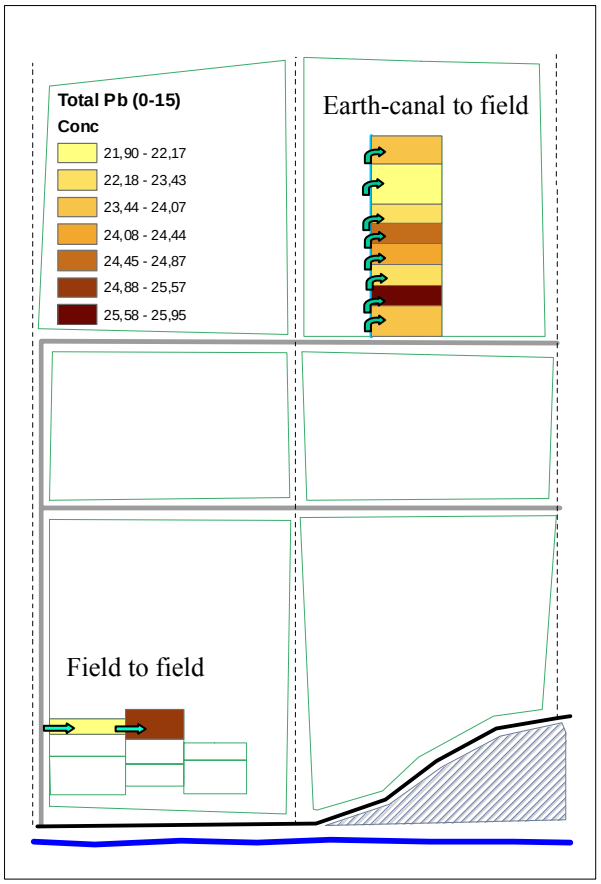

Fig. 10. Between-field distribution of AqReg Pb (mg kg^{-1}) in the 0-15 cm soil layer

The between-field distribution of AqReg metal concentrations in the 60-90 cm soil layer is shown in Fig. A2:1-4 (Appendix). AqReg Cu, Zn, Cd and Pb concentrations in all fields and depths are given in the Appendix (Tables A4:2 and A4:5).

4.1.1.1 "Earth-canal to field" irrigation

In all soil layers, except for the sediment layer which showed an opposite trend, the AqReg concentrations of Cu, Zn, Cd and Pb tended to decrease with increasing distance from the concrete canal.

4.1.1.2 "From field to field" irrigation

In the sediment layer Cu, Zn and Pb concentrations increased with increasing distance from the earth canal, although the Cd concentration decreased in the same direction. All the metals showed an increasing trend with distance in the 15-30 and 30-60 cm soil layers but a decreasing trend in the 60-90 cm layer.

4.1.2 Concentration variation between the soil depths

4.1.2.1 "Earth-canal to field" irrigation

Copper and Pb concentrations were highest in the sediment and top soil layers and decreased by depth. The Cd concentration was highest in the sediment layer, while Zn had a peak concentration in the 15-30 and 30-60 cm soil layers. Copper, Zn, Cd and Pb concentrations at different depths are shown below for gradient SG2 (Fig. 11).

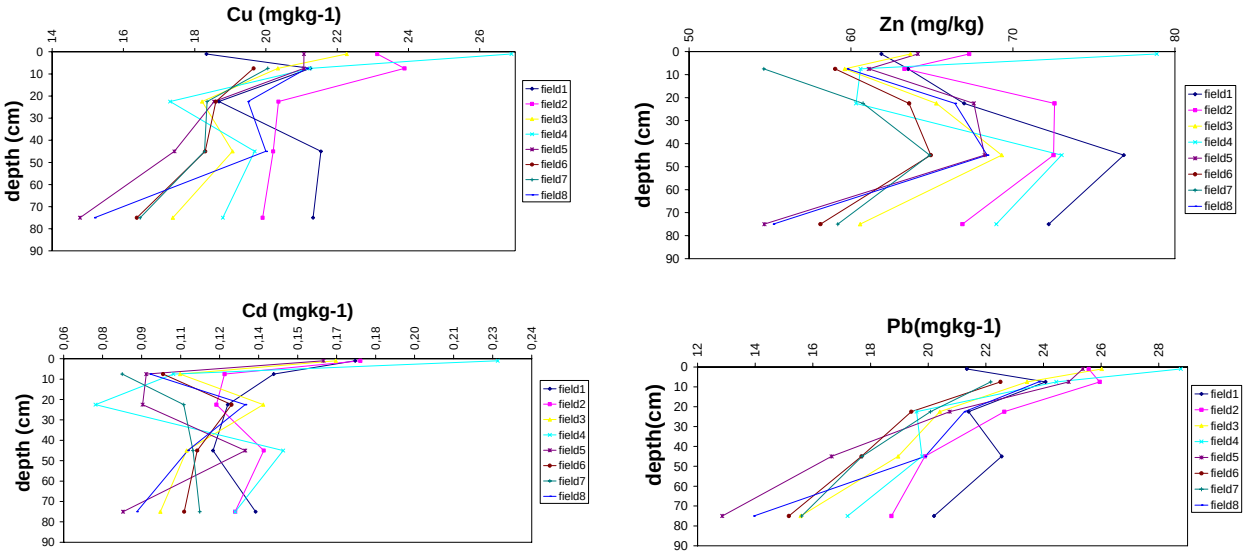

Fig. 11. AqReg concentrations of Cu, Zn, Cd and Pb at different soil depths along the SG2 gradient.

4.1.2.2 "From field to field" irrigation

The metal concentrations in the soil profile tended to decrease by depth.

4.2 Exchangeable metal concentrations

For an evaluation of the potential metal uptake by plants, concentrations of exchangeable metals are more relevant than the AqReg concentrations.

4.2.1 Distribution between the fields

Exchangeable Cu, Zn, Cd and Pb in the sediment (0-2 cm) layer are shown in Figs. 12-15.

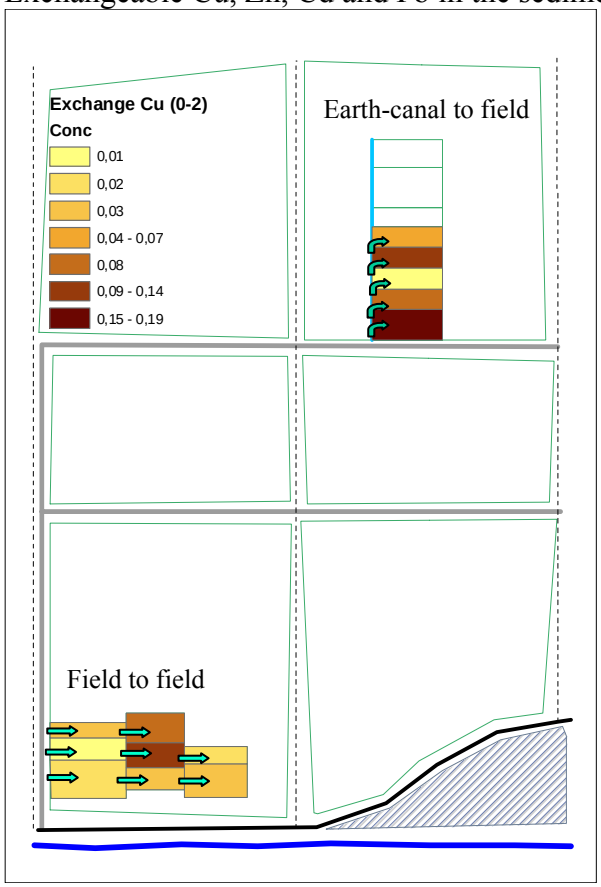

Fig. 12. Between-field distribution of exchangeable Cu (mg kg^{-1}) in the sediment (0-2 cm) layer

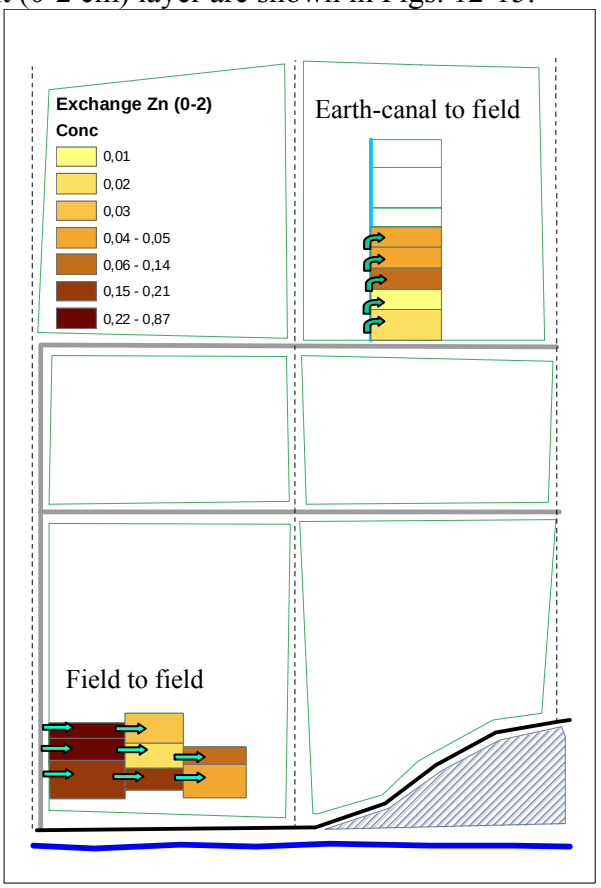

Fig. 13. Between-field distribution of exchangeable Zn (mg kg^{-1}) in the sediment (0-2 cm) layer

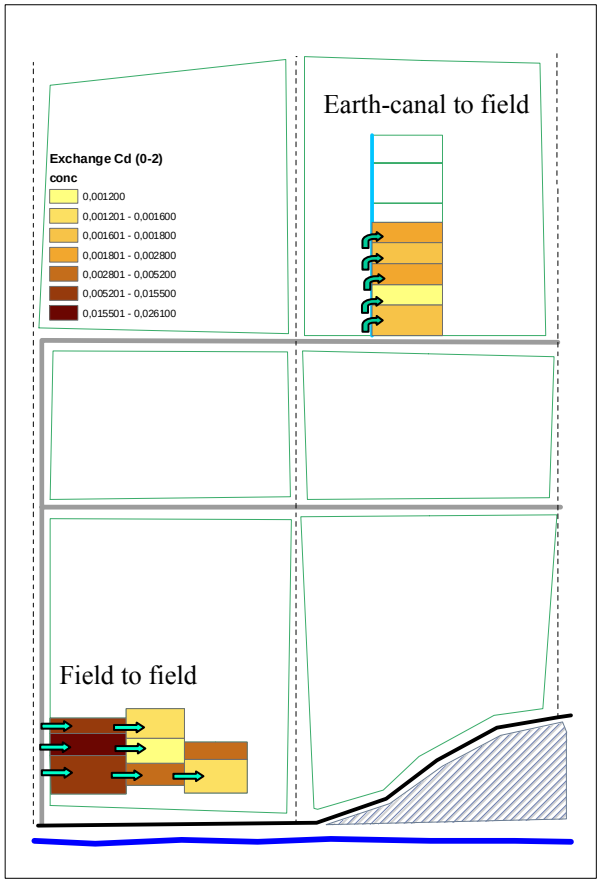

Fig. 14. Between-field distribution of exchangeable Cd (mg kg^{-1}) in the sediment (0-2 cm) layer.

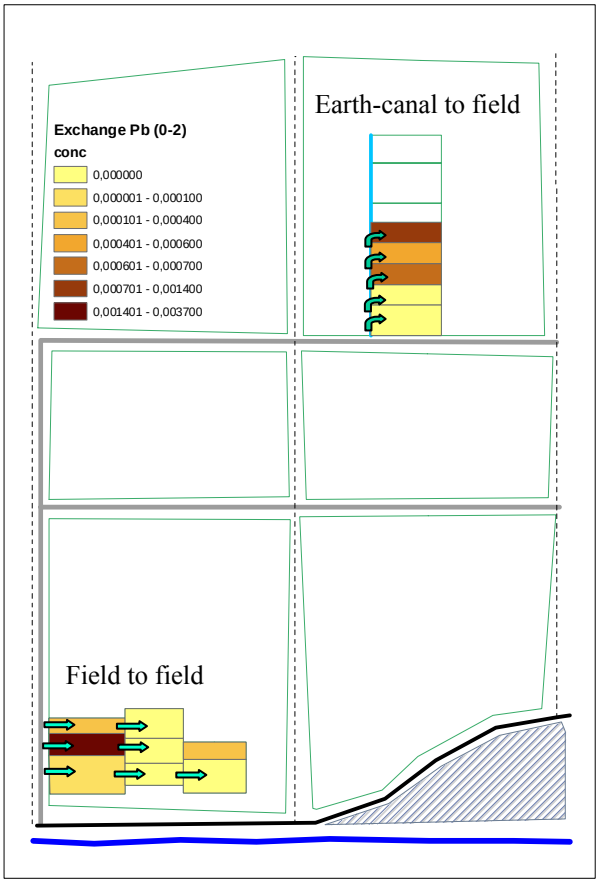

Fig. 15. Between-field distribution of exchangeable Pb (mg kg^{-1}) in the sediment (0-2 cm) layer.

Exchangeable metal concentrations of Cu, Zn, Cd and Pb in the 0-15cm soil layer are shown in Figs. 16-19.

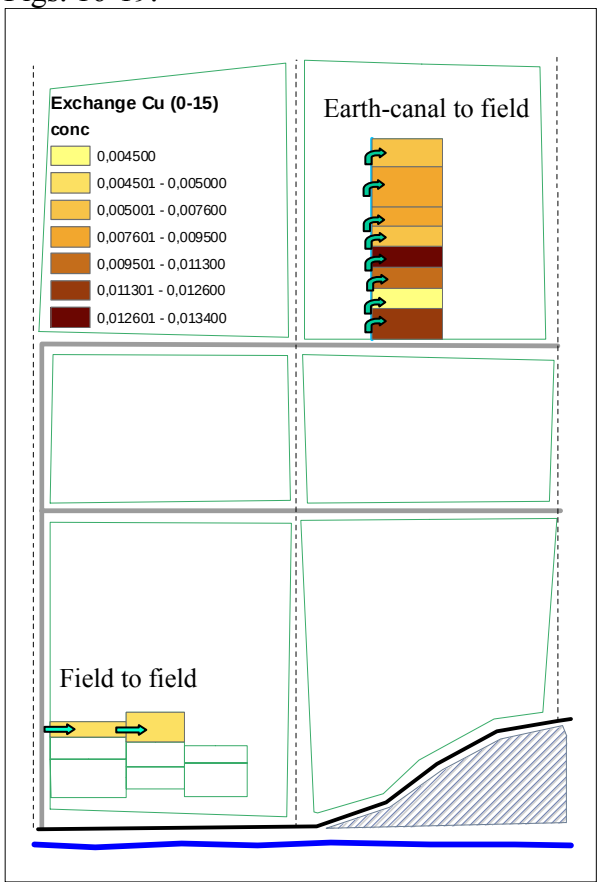

Fig. 16. Between-field distribution of exchangeable Cu (mg kg^{-1}) in the 0-15cm soil layer

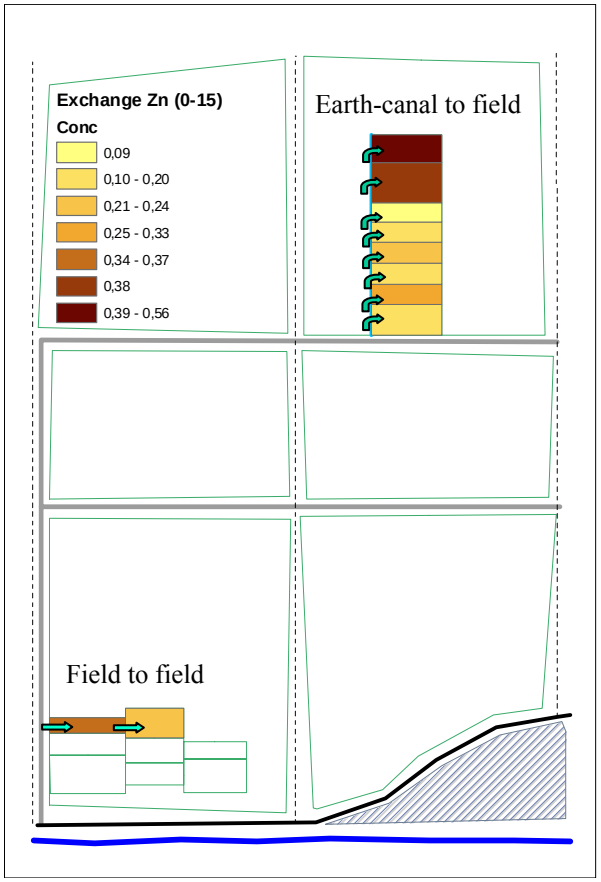

Fig. 17. Between-field distribution of exchangeable Zn (mg kg^{-1}) in the 0-15cm soil layer

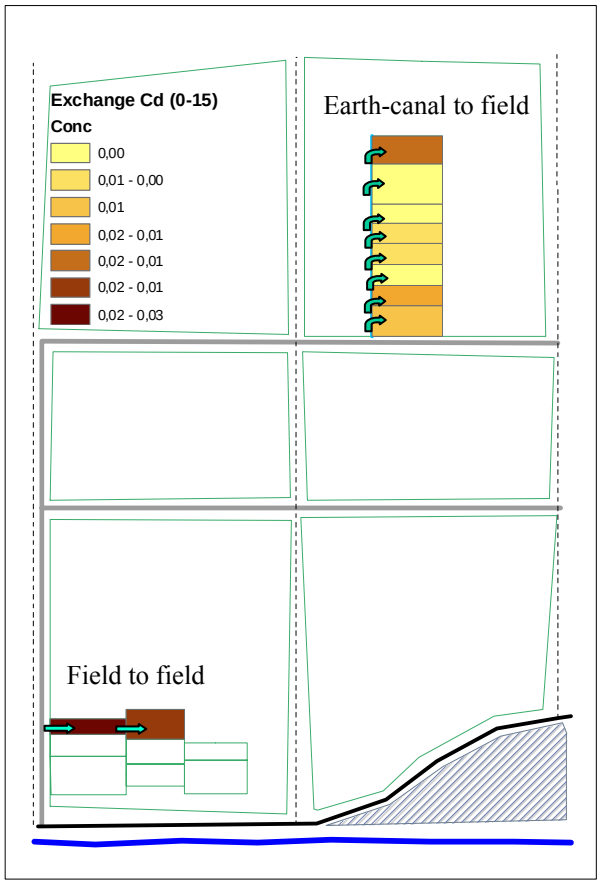

Fig. 18. Between-field distribution of exchangeable Cd (mg kg^{-1}) in the 0-15cm soil layer

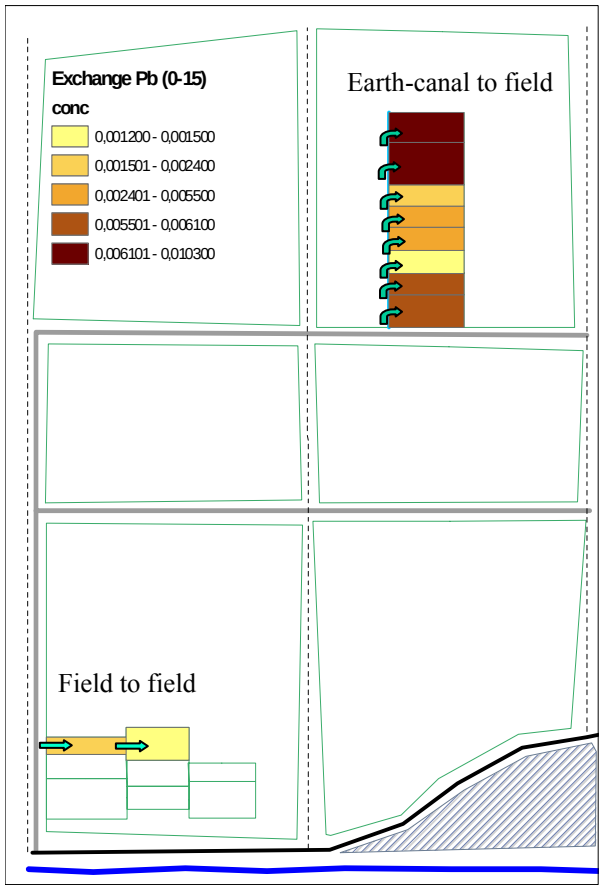

Fig. 19 Between-field distribution of exchangeable Pb (mg kg^{-1}) in the 0-15cm soil layer

The distribution of exchangeable metal concentrations between the fields in the 60-90cm soil layer (Fig. A2:5-8), and the exchangeable Cu, Zn, Cd and Pb concentrations in all fields and at all soil depths are shown in the Appendix (Tables A4:3 and A4:6).

4.2.1.1 "Earth-canal to field" irrigation

Exchangeable Cu decreased by distance from the concrete canal in all soil layers. Zinc, Cd and Pb concentrations increased by distance in the sediment and top soil layers but decreased in the two lowermost layers (30-60cm and 60-90cm).

4.2.1.2 "From field to field" irrigation

Exchangeable Cu tended to increase by distance from the concrete canal, while Zn, Cd and Pb showed weak decreasing trends.

4.2.2 Concentration pattern by soil depth

4.2.2.1 "Earth-canal to field" irrigation

In all fields, the concentration of exchangeable Cu was highest in the sediment layer, while Zn, Cd and Pb concentrations were highest in the 0-15cm soil layer. The Cu concentration was below the analytical detection limit in the two lowermost layers (30-60 and 60-90cm), while the Zn, Cd and Pb concentrations showed a slight increase in the 60-90 cm layer. The exchangeable metal concentrations at different soil depths along the SG2 gradient are shown in Fig. 20.

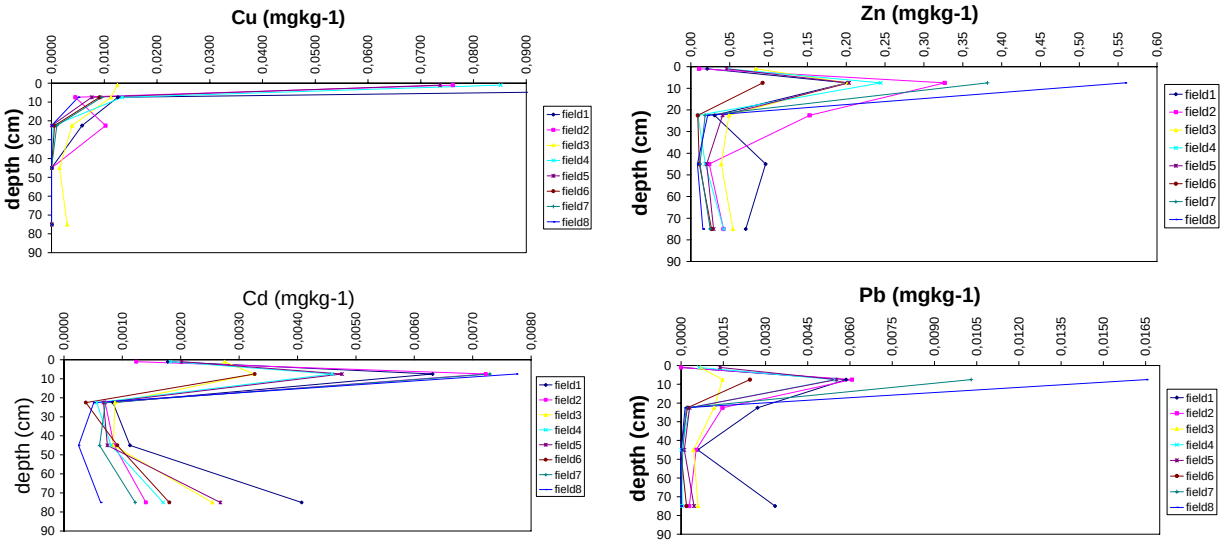

Fig. 20. Exchangeable concentrations of Cu, Zn, Cd and Pb at different soil depths along the SG gradient.

4.2.2.2 "From field to field" irrigation

Exchangeable metal concentrations tended to decrease with increasing soil depth.

4.3 Exchangeable/AqReg metal ratio

Exchangeable Cu, Zn, Cd and Pb in soil and sediment samples, were divided by the corresponding AqReg metal concentrations. The lowest and highest ratios, as well as the mean ratio of each metal are shown in Table 6.

Table 6. The lowest and highest exchangeable metal/AqReg metal concentration ratios, as well as the mean ratio for each metal in soil and sediment samples in the Bang B village.

	Cu	Zn	Cd	Pb
Lowest exch./AqReg. Ratio	(a)	0.0001	0.0023	(a)
Highest exch./AqReg ratio	0.0110	0.0108	0.1116	0.0007
Mean exch./AqReg. Ratio	0.0012	0.0015	0.0208	0.0001

(a) The lowest exchangeable Cu and Pb concentrations were below the detection limits.

4.4 pH and EC

4.4.1 Distribution between fields

4.4.1.1 "Earth canal to field" irrigation

The sediment and topsoil pH values decreased by increasing distance from the concrete canal, while pH increased by increasing distance in the lowermost soil layer (60-90cm). In the sediment layer, as well as in the 0-15 and 60-90 cm soil layers, EC decreased by increasing distance from the concrete canal (Fig. A3:1-6).

4.4.1.2 "From field to field" irrigation

In all soil layers pH increased by increasing distance from the concrete canal. In the top sediment layer there was a slight decrease in EC by increasing distance from the earth canal (Fig. A3:1-6).

4.4.2 Variation between the depths

4.4.2.1 "Earth canal to field" irrigation

Generally, pH was higher in the sediment layer compared to the 0-15 cm soil layer. At greater soil depths, pH increased by depth, except for a slight decrease in the lowermost (60-90 cm) soil layer. The mean pH value of all soil and sediment samples was 7.3 in water suspension and 6.4 in 0.01 M $CaCl_2$. In all fields EC decreased by depth throughout the soil profiles. In Fig. 21 pH ($CaCl_2$ suspensions) and EC values at different soil depths are shown for the SG2 gradient.

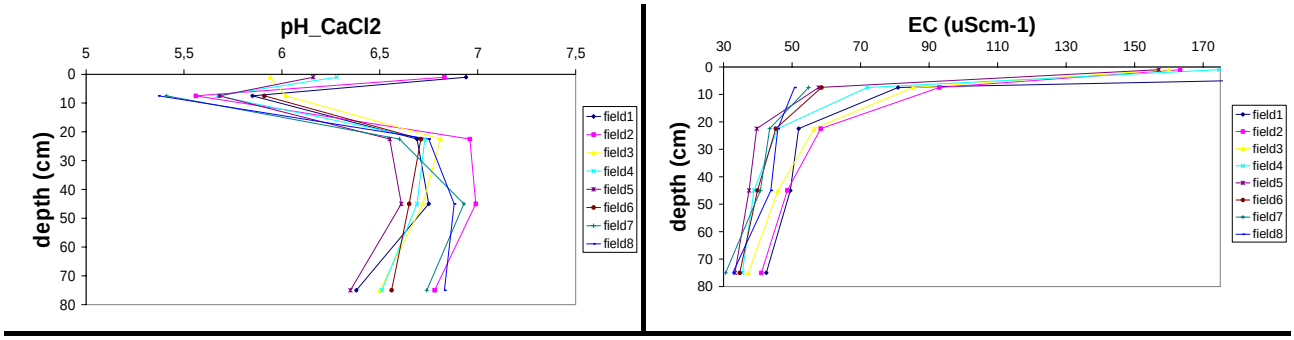

Fig. 21. pH $_{CaCl2}$ and EC at different soil depths along the SG2 gradient

4.4.2.2 "From field to field" irrigation

Except for one high pH value in the BB2 field, pH tended to increase by soil depth, while EC decreased.

4.5 Carbon and nitrogen

Organic carbon was highest in the sediment layer and decreased by increasing soil depth (Fig. 22). There was no relationship between organic C content and the distance from the concrete canal. As expected, the total N content was also highest in the sediment layer and decreased by increasing soil depth (Fig. 22).

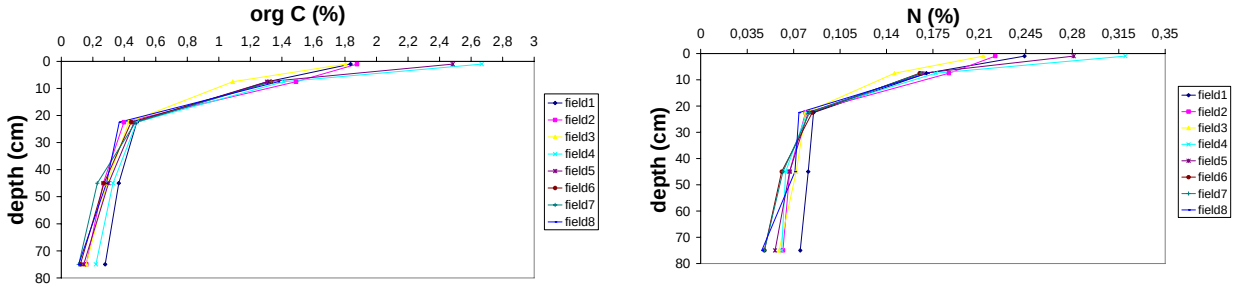

Fig. 22. Organic C and N (% dry weight) at different soil depths along the SG2 gradient

4.6 Water analyses

4.6.1 EC, COD and total suspended solids

EC, COD and total suspended solids were all high in the waste water. EC ranged from 445 to 1080 µS m^{-1}, COD varied between 11.7 and 215.6 mg O_2 L^{-1}. Total suspended solids ranged between 458 and 560 mgl^{-1} and pH varied between 7.1 and 7.6.

Within-field measurements during pumping showed that EC, COD and total suspended solids in the waste water increased along the flow path. It was not possible to find any relationship between EC, COD or total suspended solids on one hand, and specific fields, concrete canals or earth canals on the other.

4.7 Statistical analyses

Regarding the metal concentrations along the horisontal SG1 and SG2 gradients, there were no statistically significant differences between fields according to the Bonferroni simultaneous tests, while significant differences were found between soil depths. Within the horisontal SG2 gradient, Pb showed the most pronounced vertical gradient. Within both horizontal gradients exchangeable metals varied significantly by soil depth. This trend was most strongly pronounced for Pb in SG1.

In the appendix (Figs. A1:4, A1:6 and A1:8) pairs of fields or soil depths with a 95 percent significance level or more share the same prefix. Figs. A1:1-8 show calculated mean values, standard deviations and number of plots for AqReg and exchangeable metal concentrations. Fig. 23 below shows the soil profile variability with respect to AqReg Cu and Pb .

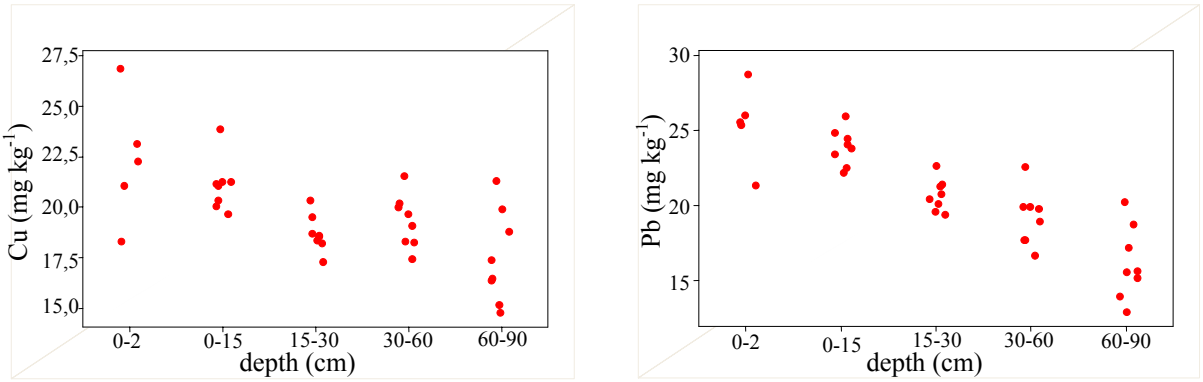

Fig. 23. Plot diagram of measured AqReg Cu and Pb concentrations versus soil depth.

4.8 Crosschecking with NISF data

Cu and Zn analyses run at SLU showed lower concentrations than analyses made at NISF (Table 7). The Cd concentration in the soil, and the concentrations of Cd and Pb in plants analysed at NISF were not available due to lack of proper analytical equipment.

Table 7. Crosschecking of AqReg metal concentrations in soil samples (0-15 cm) from the Bang B plots BB1 and BB2 analyzed at NISF and at SLU.

	Cu (mg kg^{-1})	Zn (mg kg^{-1})	Cd (mg kg^{-1})	Pb (mg kg^{-1})
Sediment (0-2cm) (SLU)				
BB1	20.2	72.5	0.25	25.9
BB2	22.3	63.7	0.16	26.0
Soil (0-15cm) (SLU)				
BB1	20.7	71.8	0.20	25.6
BB2	20.3	59.6	0.10	23.4
Soil (0-15cm) (NISF)				
BB1	23.1	84.4	-	25.8
BB2	27.4	87.7	-	32.0
Aquatic vegetables (NISF)				
BB1				
Water cress	9.5	43.7	-	-
Morning glory	15.5	61.3	-	-
BB2				
WaterCelery	17.2	63.0	-	-
Morning glory	14.8	65.8	-	-

Transfer coefficients
The transfer coefficient of Cu (total Cu concentration in above ground biomass divided by the AqReg concentration of Cu in the soil) varied between 0.46 and 0.85. In a similar manner Zn ranged between 0.61 and 1.1.

5 Discussion

5.1 Soil and sediment

5.1.1 Accumulation of trace metals

The concentrations of AqReg and exchangeable trace metals were highest in the sediment and top soil layers, indicating a trace metal accumulation due to anthropogenic inputs including the use of waste water for irrigation purposes. The urbanization in Hanoi proceeds rapidly and the population number as well as the area of industrial land are continuously increasing. In a longer time perspective, the accumulation of trace metals in arable soils around Hanoi might increase above maximum permissible levels. Therefore, a proper treatment of the irrigation waste water is necessary.

5.1.2 Complex distribution

There was a complex concentration pattern with respect to differences between individual metals, soil depths and irrigation systems. Pair wise comparisons of means with the Bonferroni simultaneous tests showed no statistically significant differences between the fields, while there were significant differences between soil depths. In the top sediment layer, there was a greater variation in concentration between the fields compared to deeper soil layers. This might be explained by the extensive soil mixing made by the farmers, together with other factors such as application of metal-containing soil amenders, fertilisers and other agro-chemicals (Kvamme and Valhed, 2004; Nguyen Manh Khai et al., 2006). Increasing metal concentrations with increasing distance from the concrete canal might be associated with the pumping of waste-water. During the observed pumping events, COD and total suspended solids in the water increased along the water pathway across the field due to turbulence. As for the suspended solids, metals might be transported further away along the water pathway, increasing metal concentrations with increasing distance from the concrete canal.

5.1.2.1 AqReg metal distribution in Bang B

It was possible to discern certain trends by inspecting the concentration distribution maps (Figs. 3-10 and A2:1-4). For example, the Cu, Zn and Pb concentrations in the sediment layer increased by increasing distance from the concrete canal within both irrigation systems, while in most of the soil layers the concentrations of these metals decreased by distance. This dissimilarity between sediment and soil may be partly explained by the extensive mixing and transport of sediment caused by the turbulence in the irrigation water during pumping.

5.1.2.2 Exchangeable metal distribution in Bang B

There was an even more complex distribution of the exchangeable metals with no obvious concentration gradients. However it was possible to discern some trends by inspecting the concentration distribution maps (Figs. 12-19 and A2:5-8). The Cu concentration decreased by distance from the source in all layers within the “earth canal to field” irrigation system. In the “from field to field” system the opposite trend was found. Within the “earth canal to field” irrigation system, the concentrations of Zn, Cd and Pb increased by the distance from the concrete canal in the sediment and top soil layers but decreased in the 15-30 and 30-60 cm layers. In the “from field to field” system Zn, Cd and Pb showed a weakly decreasing trend in

all layers and most fields. The distribution of exchangeable metals between the fields and depths did not have the same pattern as the AqReg metal concentrations.

5.1.2.3 pH-EC-org C-metal relationships

There were no obvious relationships between pH, metal concentration and distance from the concrete canal. However there was a positive relationship between pH and soil depth throughout the profiles. The EC in the soil decreased by distance from the concrete canal as well as by soil depth. As for pH, it was difficult to see any general relationships between EC, metal concentrations or distance from the concrete canal. The pK_a of soil organic matter tends to decrease as the ionic strength of the soil solution increases. Therefore a high EC in the soil may theoretically make the soil organic matter more acidic (McBride, s 109). This might increase the mobility of trace metals in the top soil, where the EC is high.

The mean pH of 7.3 in water suspension (6.4 in $CaCl_2$ suspension) in the soil and sediment samples (chapter 10.5.1) indicates a high availability of plant nutrients, and a low availability of most toxic metals. The mobilities of Cu, Zn, Cd and Pb are low in the neutral pH range. The very low exchangeable metal/AqReg metal concentration ratios which varied between 0.0001 and 0.1116 (Table 6) indicated that the metals were strongly bound to the soil particles. The organic C content in the top soil (2.7 % as a maximum) indicated that there could be a formation of organic-metal complexes, which would reduce the metal availability to the plants.

Zinc and Cd should have the highest transfer coefficients (total metal concentration in above ground biomass divided by AqReg soil concentration) while Cu and Pb in particular, are supposed to have low transfer coefficients. This tendency could be confirmed for Zn and Cu. It was not possible to calculate the transfer coefficients of Cd and Pb due to lack of quality assured plant data.

5.2 Water analyses

5.2.1 pH, COD and total suspended solids

The pH meter in the laboratory at the Environmental Technology Department, Hanoi University, which was available for the present project was not accurate enough and showed very variable results. Therefore pH data are not reported except for a few cases.

The water analyses did not agree with the hypothesis that COD and total suspended solids should decrease with increasing distance from the pumping source due to sedimentation. There were too many disturbing factors affecting the COD and total suspended solids values in the waste water. Organic acids originating from the crops, as well as fertilizers like urea and some pesticides could affect the COD values. Especially in the fields with shallow water depths, lots of particles were mixed into the water due to turbulence in the earth canals and fields caused by the flow of pumping water. There were also, various floating objects like plant pieces, ‘dirt’ and living organisms entering the water bottles when samples were collected. Therefore COD and total suspended solids were not good indicators of potentially high metal concentrations in waste water. In addition the conditions in the concrete canal, earth canal, and vegetable fields were not the same, which distorted the gradient from concrete canal to vegetable field. It was possible to estimate the amount of suspended solids by visual observations. Therefore a few total suspended solid analyses were made.

5.2.2 Complex pumping schedule

Another problem was to find out the pumping schedule in Bang B village. Farmers often pumped at least one day per week depending on the weather. They started in the early morning and continued until the fields had received enough water. It was very difficult to be informed in

advance about their schedule. It was complex, and there were also communication problems. Therefore I could not collect water samples as planned, i.e. at different times before, during and after pumping events. It was not possible to know in advance which field or fields they were going to irrigate, which made it difficult to make plans for the sampling.

5.3 Comparisons with results from similar studies

In order to evaluate whether the achieved results were reasonable or not, they were compared with results from other similar studies.

5.3.1 Ho Chi Minh City, Vietnam

Recent studies conducted in Vietnam showed that trace metals had accumulated in agricultural soils due to the use of waste water for irrigation. A project that was carried out in 2002 reported high soil concentrations of 'total' Cd, Cu, Zn, and Pb at 126 sampling points (Table 8) in rice fields near Ho Chi Minh City. The high concentrations indicated that the paddy soils were polluted by industrial and household waste water. According to the standard limit values used in Sweden, Canada, and UK (Table 4), Cd exceeded the permissible level at each location. The maximum concentration was 10 mg kg^{-1}. Zinc and Pb concentrations also indicated some pollution, while the Cu concentrations were within the permissible limits. Metal analyses were made with a polarographic method. (Nguyen Ngoc Quynh and Le Huy Ba, 2002)

Table 8. Total metal concentrations (mg kg^{-1}) in paddy soils polluted with waste water from Ho Chi Minh City (Nguyen Ngoc Quynh and Le Huy Ba, 2002)

Location	No. of samples	Cu	Zn	Cd	Pb
Nha Be	88	29	110	10	62
District 7	4	23	233	5	39
Binh Chanh	10	31	197	1	58
District 2	10	33	435	6	44
District 9	6	30	568	5	41
Thu Duc	8	30	282	7	44

The 'total' concentrations of all the metals shown in Table 8 are higher than the concentrations found in the Bang B village (Table 4).

5.3.2 Hanoi City, Vietnam

'Total' concentrations of trace metals were measured in 13 agricultural soils in the Tu Liem and Thanh Tri districts of Hanoi City (Ho Thi Lam Tra *et al*., 1998). In 70 percent of the samples, pH ranged between 6.0 and 7.0. According to the Swedish maximum permissible level for application of sewage sludge on agricultural soils (table 4), Cu and Zn both exceeded the standard maximum limit values in one of the fields, while Cd exceeded the limit in two fields. Metal analyses were made with a volt-ampere stripping method and atomic absorption spectrophotometry (AAS).

5.3.3 Hanoi City, Vietnam

Nine soil samples from rice fields and vegetable fields were collected in the Tu Liem and Thanh Tri districts of Hanoi City, and analyzed for total metal concentrations. Milled air dry soil samples were digested with HF, HNO_3 and $HClO_4$ and analysed by AAS. The Cu concentration varied between 40.1 and 73.2 mg kg^{-1}, Zn between 98.2 and 137.2 mg kg^{-1}, Cd between 0.16 and 0.36 mg kg^{-1} and Pb between 31.9 and 45.3 mg kg^{-1}. Compared to the standard values (Table 4), the soil showed a slight metal pollution except for Cd (Ho Thi Lam Tra and Egashira, 1999). Copper, Zn and Pb concentrations were higher than the concentrations found in the Bang B village. Cadmium concentrations in Bang B village were higher except for a few sediment samples.

5.3.4 State of Hidalgo, Mexico

Lead and Cd concentrations were measured in six agricultural soils irrigated with untreated waste water for an average period of 20 years in district 03 in the State of Hidalgo, Mexico (Lucho-Constantino *et al*., 2004). The air dried and sieved (≤2mm) soil samples were extracted by **??** and analyzed by ICP (3000XL Perkin Elmer). The pH in the soils was > 7, and the EC of the soils was regarded as moderate to moderately high. The texture was clay and sandy clay. The 'total' metal concentrations in the topsoil (0-30cm) were in the range 0.6-1.9 mg kg^{-1} (Cd) and 3.9-47 mg kg^{-1} (Pb). These data indicated a slight pollution compared to the standard limit values shown in Table 4. The Cd concentrations were greater than those found in Bang B, whilst the Pb concentrations were in the same range (Table 4).

5.3.5 State of Hidalgo, Mexico

'Total' concentrations and soluble plus exchangeable concentrations of Cu, Zn, Cd, and Pb were investigated in four soil profiles (Flores *et al*., 1997). The profiles were irrigated with waste water, which was obtained from the Rural Development district 063, State of Hidalgo, Mexico. The soil samples were air dried and ground to pass a 2 mm stainless-steel sieve. 'Total' metal concentrations were obtained by extracting with 4 M HNO_3 at 80 ºC for 12 h (extracts the same or a less amount of metals compared to Aqua Regia). Exchangeable metals were extracted by shaking extractant-soil suspensions for 2 h. The extractant was a DTPA solution consisting of 0.005 M DTPA, 0.01 M $CaCl_2$, and 0.1 M TEA adjusted to pH 7.3. All soil extracts were analyzed on a flame atomic absorption spectrophotometer equipped with a deuterium-arc background corrector (Perkin Elmer model 3110). All elements that were examined in the different profiles had a higher total concentration in the surface layers (0-10 cm) and (20-30cm), than in the two lowermost layers (50-60cm) and (90-100 cm). Except for Cd at one of the sites, and Pb at all sites, a small percentage (4.5% or less) of the total metal stock was in an easily mobile soluble plus exchangeable form. The high pH values of these soils favoured a low degree of trace metal solubility.

Table 9. Soil properties, total and exchangeable plus soluble concentrations of Cu, Zn, Cd, and Pb (mg kg^{-1}) in four different soil profiles, State of Hidalgo, Mexico. (Flores et al., 1997)

Site	Depth (cm)	pH	Org. (%)	Silt (%)	Clay (%)	Tot Cu	Exc. Cu	Tot Zn	Exc. Zn	Tot Cd	Exc. Cd	Tot Pb	Exc. Pb
3	0-10	8.65	1.47	38.8	24.9	10.5	0.49	155	105	1.28	0.05	36.1	3.70
	20-30	8.71	0.92	35.3	18.4	9.59	0.43	126	0.84	1.07	0.04	30.1	2.96
	50-60	8.70	0.39	41.3	30.4	9.23	0.31	111	0.78	0.96	0.03	24.1	3.22
	90-100	8.58	0.23	36.3	31.6	8.88	0.24	101	0.73	0.86	0.03	18.1	1.48
83	0-10	8.32	2.74	29.5	36.1	30.2	0.63	207	3.64	2.08	0.08	46.7	3.05
	20-30	8.38	2.58	-	-	29.7	0.44	191	2.36	1.82	0.07	42.2	2.29
	50-60	8.42	1.52	28,4	45.0	14.9	0.38	165	1.50	1.43	0.05	33.1	1.53
	90-100	8.53	1.26	56.7	29.3	13.2	0.25	158	0.43	1.04	0.03	19.6	1.53
119	0-10	8.21	2.92	33.3	58.0	23.3	0.51	186	4.26	2.67	0.07	47.6	4.66
	20-30	8.24	2.69	38.3	51.4	20.2	0.51	139	3.61	2.27	0.07	43.2	3.11
	50-60	8.32	1.87	39.3	45.4	15.7	0.51	130	2.59	1.74	0.05	32.7	2.72
	90-100	8.40	1.71	37.3	37.4	11.6	0.25	121	0.87	1.20	0.02	23.8	1.55
183	0-10	7.86	4.05	44.6	20.3	86.5	0.77	236	6.38	5.07	0.13	131	5.47
	20-30	8.19	1.93	34.4	29.4	42.8	0.64	170	3.53	3.12	0.07	77.8	3.91
	50-60	8.25	1.13	49.5	36.4	19.1	0.51	142	1.15	2.60	0.04	35.9	3.13
	90-100	8.34	0.48	10.6	8.36	12.6	0.38	107	0.86	2.08	0.03	25.5	2.74

The ‘total’ metal concentrations shown in Table 9 indicate an accumulation and some pollution in relation to the maximum permissible levels shown in Table 4. Total Zn, Cd and Pb concentrations were greater than the concentrations found in Bang B, whilst the Cu concentrations were in the same range. Concentrations of exchangeable metals were greater than those found in Bang B.

5.3.6 Al-Lajoun Valley, Karak, Jordan

A field study was conducted to determine the concentrations of Cu, Zn and Pb in untreated waste water and soil near Al-Lajoun Valley, Karak, Jordan (Jiries *et al*., 2002). 45 soil samples (0-25cm) and 20 plant samples were collected in an area used for studies of the disposal of untreated waste water. Samples of about one gram of dried and sieved (≤2mm) soil were extracted overnight with 10 ml 50 % HNO_3 solution. The samples were ultrasonicated for one hour and heated in a test tube heater at 90 ºC for another hour. The final extracts were filtered and diluted with 1% HNO_3. Metal analyses were made on a flame atomic absorption spectrophotometer (Varian Spectr AA 800) equipped with a deuterium lamp background correction. The trace metals had relatively higher concentrations in the soil than in the waste water which might indicate a metal accumulation in the soil (or presence of metals in the parent material). The metal concentrations were at their highest levels at the point where the waste water was introduced. They decreased gradually with increasing distance from this point.

5.3.7 Comparison between the case studies on metals in waste water irrigated soils

The six case studies described above showed almost consistently higher concentrations of trace metals compared to the Bang B village. There were just a few exceptions. This could be explained by the short time period during which the inhabitants of the Bang B village have used waste water for irrigation. A contributing reason could be that Hanoi is in a rather early stage of industrial development with rather few factories that could emit trace metals into the water. The lower concentrations could perhaps be explained by a better quality of the laboratory analyses in this thesis, resulting in a higher accuracy at low concentrations. Because Cd usually is present at low concentrations in the soil, analyses with flame atomic absorption spectrophotometry, might not be accurate enough for determination of Cd concentrations in the soil.

6 Conclusion

Compared to maximum permissible international levels, AqReg Cu, Zn, Cd and Pb were within the standards. The solubility of the trace metals was very low, indicating that the metals were strongly bound to the soil particles. The very complex distribution of metals between the fields indicated that the short distance from the water input source to the fields, the great variation in amounts of irrigation water together with many other disturbing factors, made the monitoring at a smaller scale very difficult. The water analyses were difficult to carry out due to great variations in irrigation water quality, flow velocity and pathways. The expected pattern of decreasing concentrations with increasing distance from the concrete canal was not found in all cases. There was a positive relationship between decreasing concentration and soil depth, however. This indicated an accumulation of trace metals in the topsoil due to anthropogenic input sources including the use of waste water. The differences between the two irrigation systems “from earth-canal to field” and “from field to field” were complex and difficult to evaluate. Variations in decreasing or increasing metal concentrations with distance from the water input source indicated that there were real differences between the two systems. However it was difficult to say which of the systems should be preferred.

As mentioned, trace metal concentrations were still below the maximum permissible levels. However, the accumulation of metals in the soil due to the use of waste water for irrigation is

expected to increase as urbanization and industrialization of Hanoi continue to increase. Higher amounts of metals could eventually lead to undesirable transfer into the human food chain and in the long term cause risks for human diseases as well as phytotoxicity and negative impact on soil fertility. Even though there are benefits with waste water irrigation, pre-treatment of the waste water in Bang B village would be necessary for a future sustainable development.

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9 Appendix

Appendix 1. Statistical calculations

Calculated mean values (Mean), standard deviation (StDev) and number of plots (n). Fields or depths that showed statistically significant differences share the same prefix.

Table A1:1. Gradient SG1: Pair wise comparisons showed no significant between-field differences in AqReg metal concentrations.

	Field	Mean	StDev	n
Cu	1	20.4	1.10	5
	2	21.1	3.12	5
Zn	1	71.6	3.63	5
	2	72.0	8.34	5
Cd	1	0.21	0.13	5
	2	0.18	0.06	5
Pb	1	20.5	1.83	5
	2	22.6	4.28	5

Table A1:2. Pair wise comparisons showed no statistically significant differences of the AqReg metal concentrations between the five soil depths in gradient SG1.

	Depth	Mean	StDev	n
Cu	0-2	19.8	19.8	2
	0-15	20.6	20.6	2
	15-30	23.3	23.3	2
	30-60	22.0	22.1	2
	60-90	18.0	18.0	2
Zn	0-2	74.3	2.54	2
	0-15	71.9	0.22	2
	15-30	75.2	1.99	2
	30-60	75.1	7.89	2
	60-90	62.7	5.83	2
Cd	0-2	0.33	0.12	2
	0-15	0.23	0.04	2
	15-30	0.15	0.03	2
	30-60	0.14	0.03	2
	60-90	0.10	0.01	2
Pb	0-2	23.9	2.85	2
	0-15	23.7	2.59	2
	15-30	22.3	1.62	2
	30-60	21.2	2.08	2
	60-90	16.5	1.59	2

Table A1:3. Pair wise comparisons of the AqReg metal concentrations between the eight fields in gradient SG2 showed no statistically significant differences between the fields.

	Field	Mean	StDev	n
Cu	1	20.2	1.58	**5**
	2	21.5	1.86	**5**
	3	19.5	1.92	**5**
	4	20.8	3.70	**5**
	5	18.6	2.65	**5**
	6	18.2	1.37	**4**
	7	18.3	1.46	**4**
	8	**19.0**	**2.61**	**4**

	Field	Mean	StDev	n
Zn	1	68.3	6.21	5
	2	68.5	3.99	5
	3	63.7	3.89	5
	4	68.4	8.03	5
	5	63.1	5.55	5
	6	61.4	3.35	4
	7	59.9	4.23	4
	8	62.5	6.08	4

	Field	Mean	StDev	n
Cd	1	0.138	0.022	5
	2	0.136	0.023	5
	3	0.122	0.028	5
	4	0.134	0.058	5
	5	0.111	0.033	5
	6	0.110	0.011	4
	7	0.103	0.014	4
	8	0.105	0.019	4

	Field	Mean	StDev	n
Pb	1	21.9	1.47	5
	2	22.6	3.25	5
	3	20.9	4.03	5
	4	22.0	4.62	5
	5	20.1	5.37	5
	6	18.7	3.08	4
	7	18.9	2.85	4
	8	19.7	4.19	4

Table A1:4. Pair wise comparisons of the AqReg metal concentrations between the five soil depths in gradient SG2 showed some statistically significant differences

	Index	Depth	Mean	StDev	n
Cu	a	0-2^{ce}	22.3	3.12	5
	b	0-15^{e}	21.1	1.29	8
	c	15-30^{a}	18.7	0.90	8
	d	30-60	19.3	1.31	8
	e	60-90^{ab}	17.5	2.30	8

	Index	Depth	Mean	StDev	n
Zn	a	0-2	67.2	6.83	5
	b	0-15^{d}	60.2	2.79	8
	c	15-30	65.4	3.97	8
	d	30-60^{eb}	69.8	4.14	8
	e	60-90^{d}	62.0	6.57	8

	Index	Depth	Mean	StDev	n
Cd	a	0-2^{bcde}	0.180	0.027	5
	b	0-15^{a}	0.104	0.019	8
	c	15-30^{a}	0.113	0.022	8
	d	30-60^{a}	0.121	0.015	8
	e	60-90^{a}	0.109	0.019	8

	Index	Depth	Mean	StDev	n
Pb	a	0-2^{cde}	25.4	2.66	5
	b	0-15^{cde}	23.9	1.23	8
	c	15-30^{abe}	20.7	1.06	8
	d	30-60^{abe}	19.1	1.84	8
	e	60-90^{abcd}	16.2	2.43	8

Table A1:5. Pair wise comparisons of the exchangeable metal concentrations between the two different fields in gradient SG1 showed no statistically significant differences.

	Field	Mean	StDev	n
Cu	1	0.0070	0.0131	5
	2	0.0186	0.0332	5
Zn	1	0.1342	0.1551	5
	2	0.0703	0.0928	5
Cd	1	0.0105	0.0120	5
	2	0.0036	0.0035	5
Pb	1	0.0004	0.0008	5
	2	0.0003	0.0005	5

Table A1:6. Pair wise comparisons of the exchangeable metal concentrations between the five different soil depths in gradient SG1 showed some significant differences concerning Pb.

	Index	Depth	Mean	StDev	n
Cu	a	0-2	0.0539	0.0337	2
	b	0-15	0.0050	0.0000	2
	c	15-30	0.0045	0.0064	2
	d	30-60	0.0007	0.0010	2
	e	60-90	0.0000	0.0000	2

	Index	Depth	Mean	StDev	n
Zn	a	0-2	0.1256	0.1372	2
	b	0-15	0.3006	0.0935	2
	c	15-30	0.0385	0.0193	2
	d	30-60	0.0227	0.0034	2
	e	60-90	0.0239	0.0110	2

	Index	Depth	Mean	StDev	n
Cd	a	0-2	0.0084	0.0100	2
	b	0-15	0.0194	0.0140	2
	c	15-30	0.0034	0.0008	2
	d	30-60	0.0026	0.0002	2
	e	60-90	0.0016	0.0006	2

	Index	Depth	Mean	StDev	n
Pb	a	0-2[b]	0.0002	0.0003	2
	b	0-15[acde]	0.0015	0.0004	2
	c	15-30[b]	0.0001	0.0001	2
	d	30-60[b]	0.0000	0.0000	2
	e	60-90[b]	0.0002	0.0002	2

Table A1:7. Pair wise comparisons of the exchangeable metal concentrations between the eight different fields in gradient SG2 showed no statistically significant differences.

	Field	Mean	StDev	n
Cu	1	0.0440	0.0883	5
	2	0.0182	0.0327	5
	3	0.0064	0.0051	5
	4	0.0198	0.0370	5
	5	0.0163	0.0323	5
	6	0.0024	0.0045	4
	7	0.0026	0.0046	4
	8	0.0013	0.0026	4

	Field	Mean	StDev	n
Zn	1	0.0838	0.0721	5
	2	0.1111	0.1330	5
	3	0.0855	0.0669	5
	4	0.0722	0.0975	5
	5	0.0680	0.0764	5
	6	0.0347	0.0393	4
	7	0.1092	0.1818	4
	8	0.1510	0.2720	4

	Field	Mean	StDev	n
Cd	1	0.0028	0.0023	5
	2	0.0023	0.0028	5
	3	0.0021	0.0011	5
	4	0.0019	0.0016	5
	5	0.0022	0.0017	5
	6	0.0016	0.0013	4
	7	0.0025	0.0032	4
	8	0.0023	0.0037	4

	Field	Mean	StDev	n
Pb	1	0.0025	0.0024	5
	2	0.0017	0.0025	5
	3	0.0009	0.0005	5
	4	0.0013	0.0023	5
	5	0.0015	0.0023	5
	6	0.0007	0.0011	4
	7	0.0027	0.0051	4
	8	0.0042	0.0082	4

Table A1:8. Pair wise comparisons of the exchangeable metal concentrations between the five different depths in gradient SG2 showed some statistically significant differences for all metals.

	Index	Depth	Mean	StDev	n
Cu	a	0-2^{bcde}	0.0899	0.0689	5
	b	0-15^{a}	0.0091	0.0033	8
	c	15-30^{a}	0.0027	0.0037	8
	d	30-60^{a}	0.0002	0.0005	8
	e	60-90^{a}	0.0004	0.0011	8

	Index	Depth	Mean	StDev	n
Zn	a	0-2^{b}	0.0415	0.0282	5
	b	0-15^{acde}	0.2763	0.1439	8
	c	15-30^{b}	0.0414	0.0472	8
	d	30-60^{b}	0.0286	0.0289	8
	e	60-90^{b}	0.0382	0.0179	8

	Index	Depth	Mean	StDev	n
Cd	a	0-2^{b}	0.0019	0.0006	5
	b	0-15^{acde}	0.0056	0.0018	8
	c	15-30^{b}	0.0007	0.0002	8
	d	30-60^{b}	0.0008	0.0002	8
	e	60-90^{b}	0.0020	0.0011	8

	Index	Depth	Mean	StDev	n
Pb	a	0-2^{b}	0.0005	0.0006	5
	b	0-15^{acde}	0.0067	0.0048	8
	c	15-30^{b}	0.0008	0.0009	8
	d	30-60^{b}	0.0002	0.0003	8
	e	60-90^{b}	0.0006	0.0011	8

Appendix 2. Distribution of metal concentrations between the fields

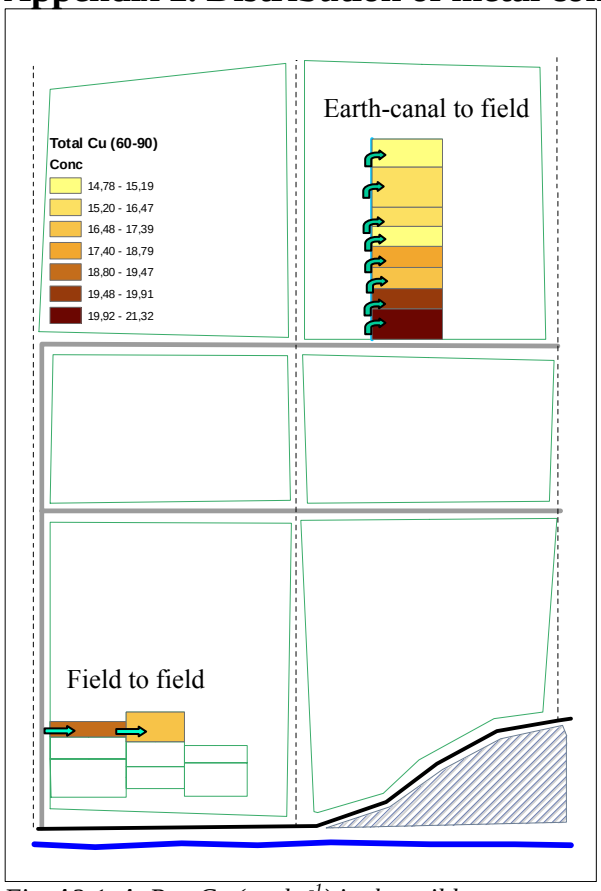

Fig. A2:1. AqReg Cu (mg kg^{-1}) in the soil layer (60-90cm)

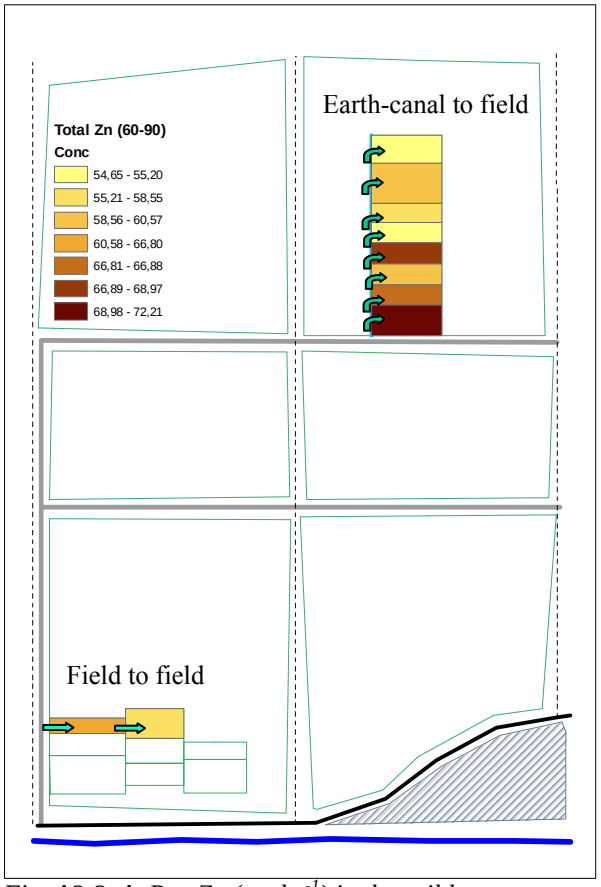

Fig. A2:2. AqReg Zn (mg kg^{-1}) in the soil layer (60-90cm)

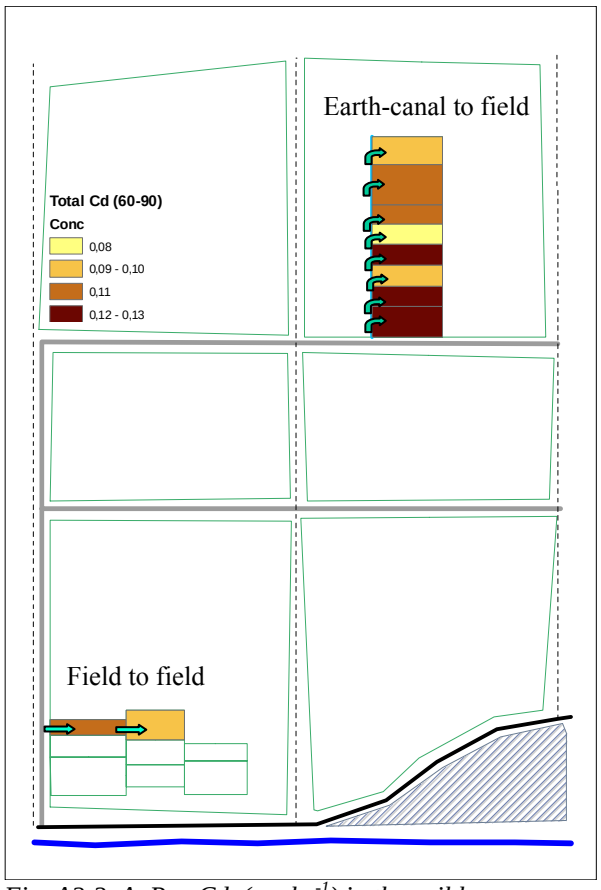

Fig. A2:3. AqReg Cd (mg kg^{-1}) in the soil layer (60-90cm)

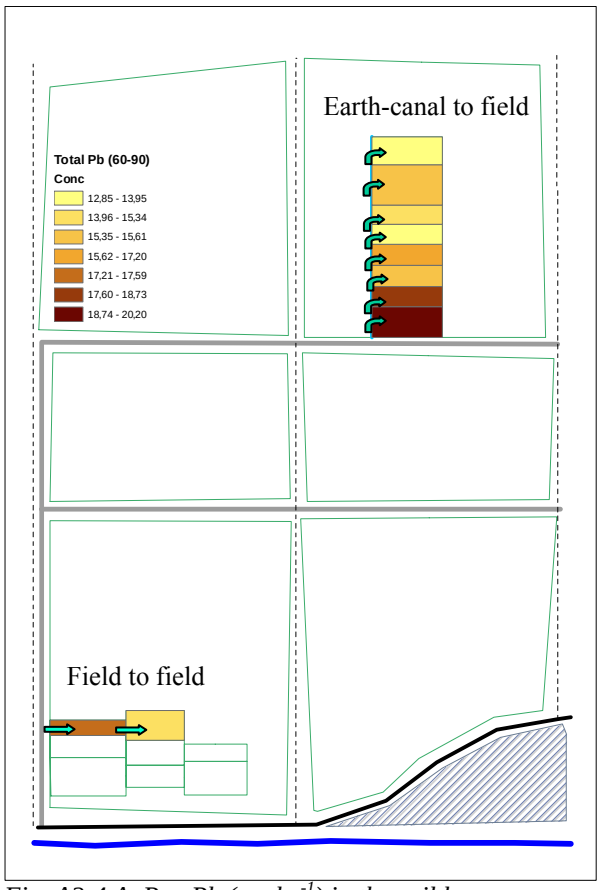

Fig. A2:4.AqReg Pb (mg kg^{-1}) in the soil layer (60-90cm)

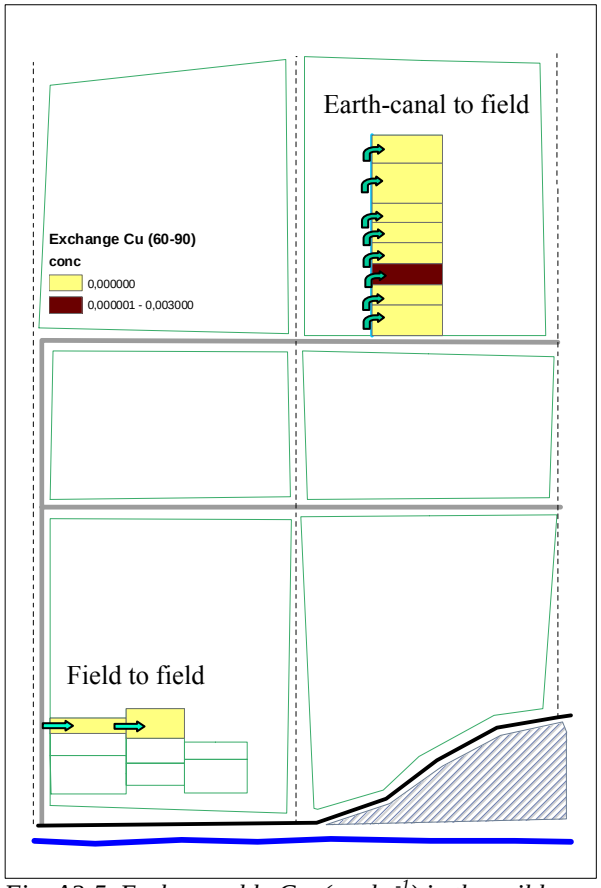

Fig. A2:5. Exchangeable Cu (mg kg^{-1}) in the soil layer (60-90cm)

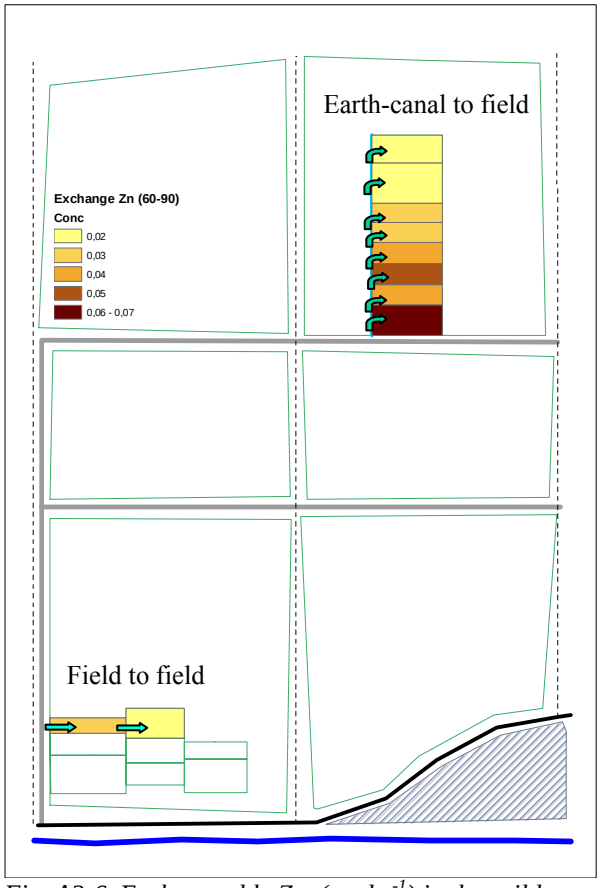

Fig. A2:6. Exchangeable Zn (mg kg^{-1}) in the soil layer (60-90cm)

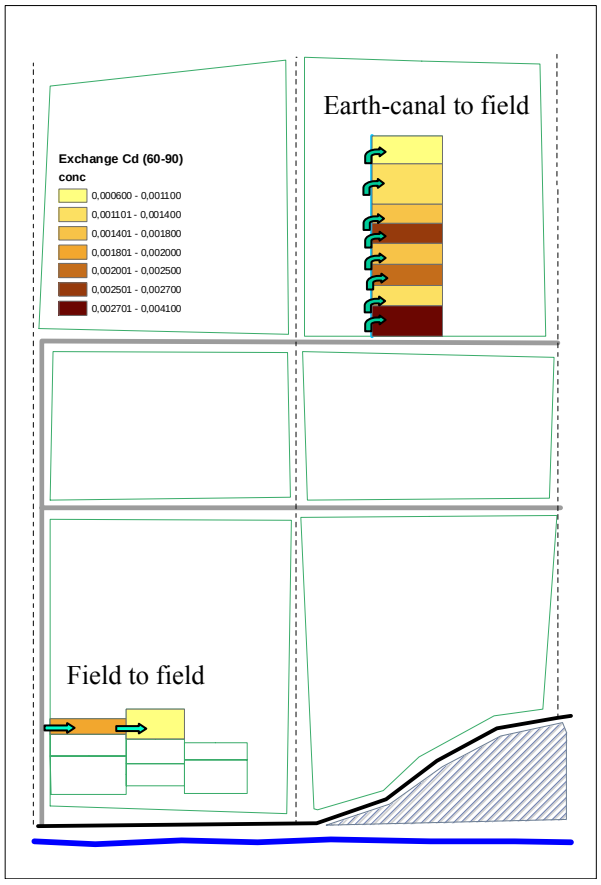

Fig. A2:7. Exchangeable Cd (mg kg^{-1}) in the soil layer (60-90cm)

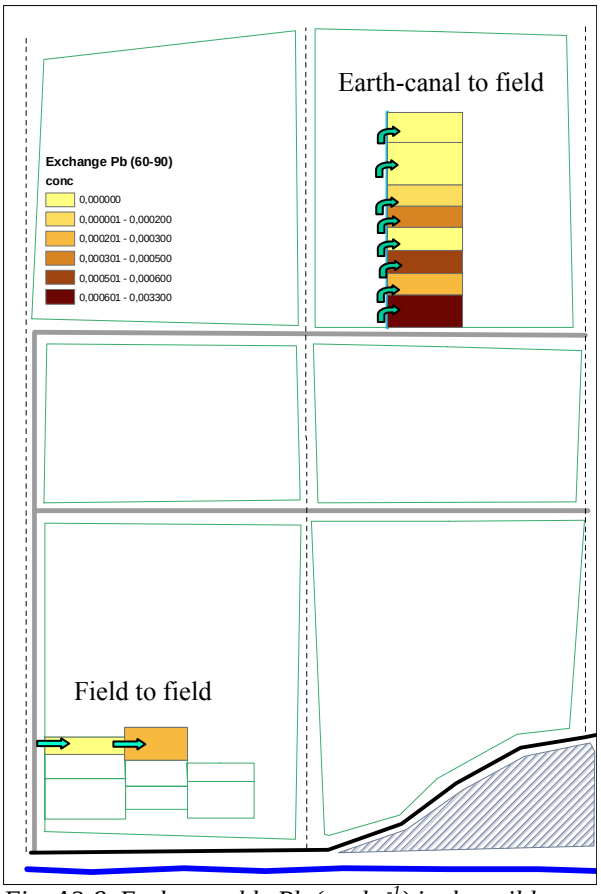

Fig. A2:8. Exchangeable Pb (mg kg^{-1}) in the soil layer (60-90cm)

Appendix 3 Distribution of EC and pH between the fields

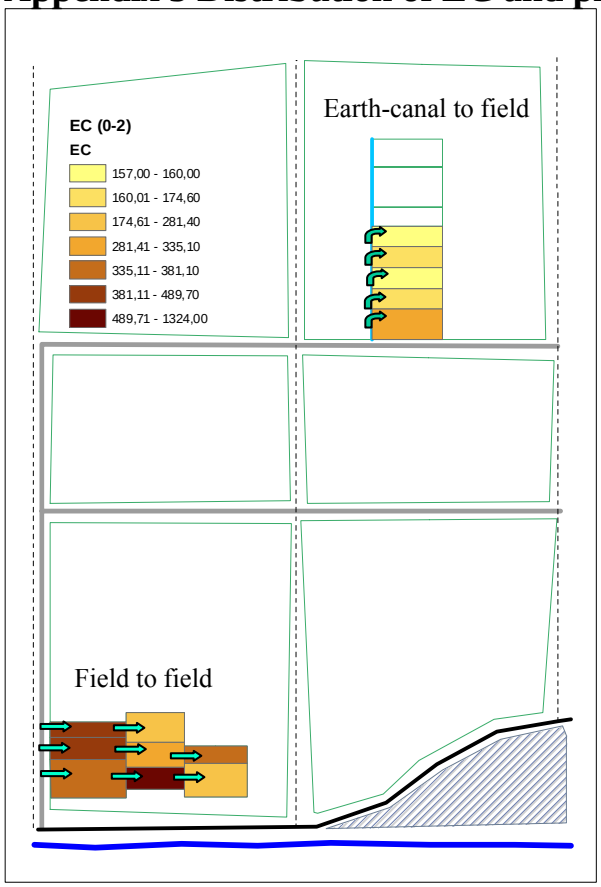

Fig. A3:1. EC in the sediment layer (0-2 cm)

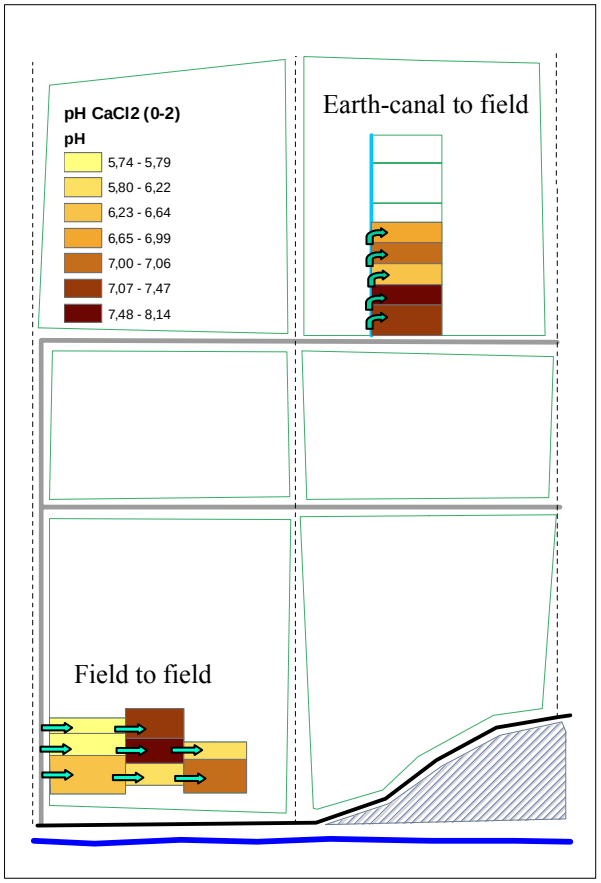

Fig. A3:2. pH in the sediment layer (0-2 cm)

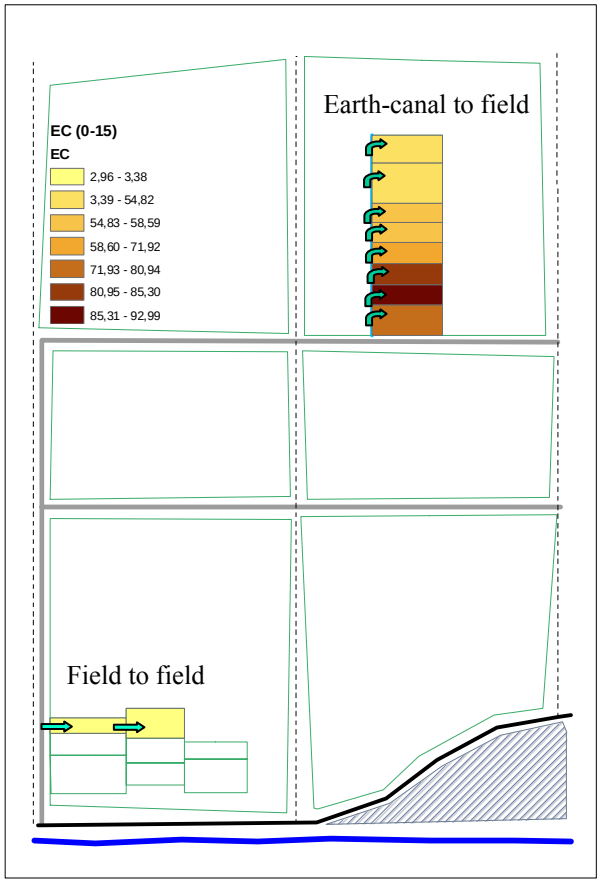

Fig. A3:3. EC in the top soil layer layer (0-15) cm

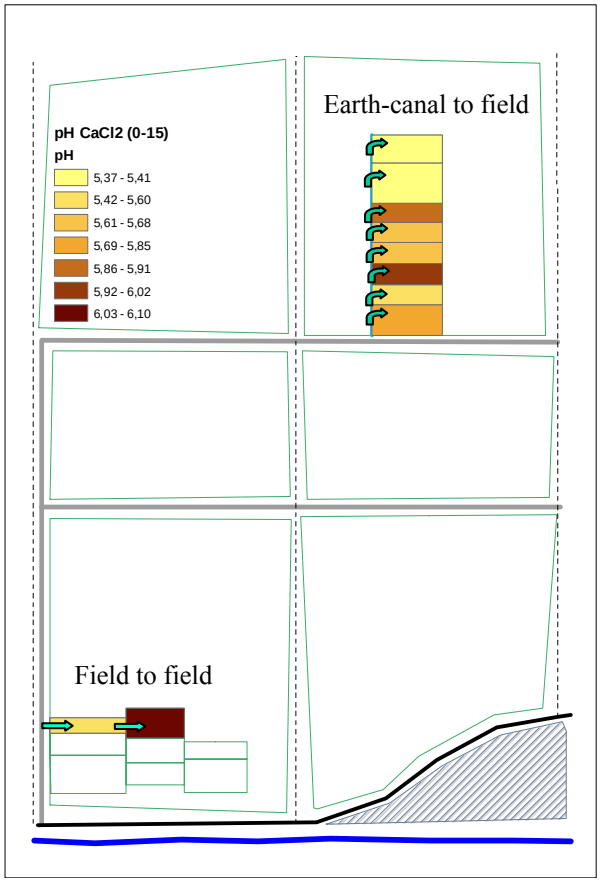

Fig. A3:4. pH in the top soil layer layer (0-15 cm)

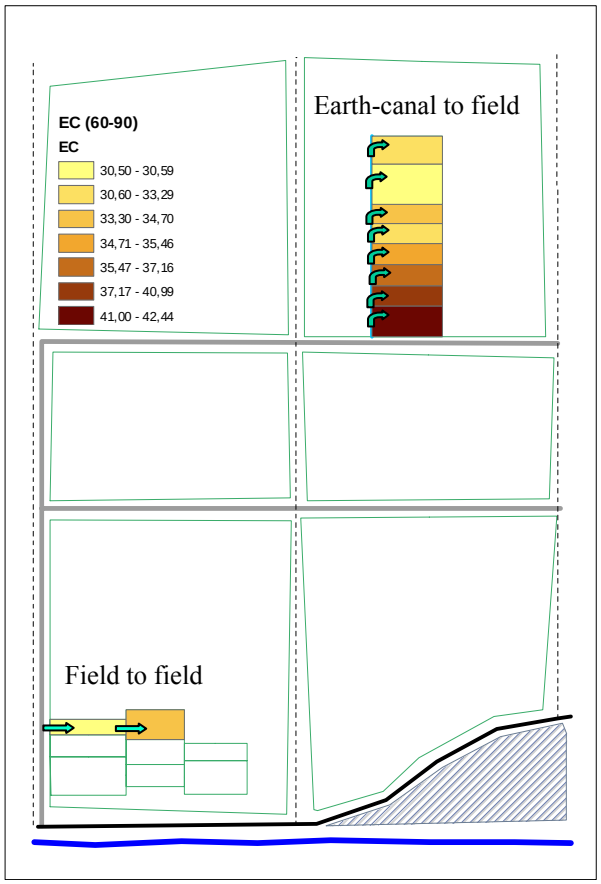

Fig. A3:5. EC in the soil layer 60-90cm

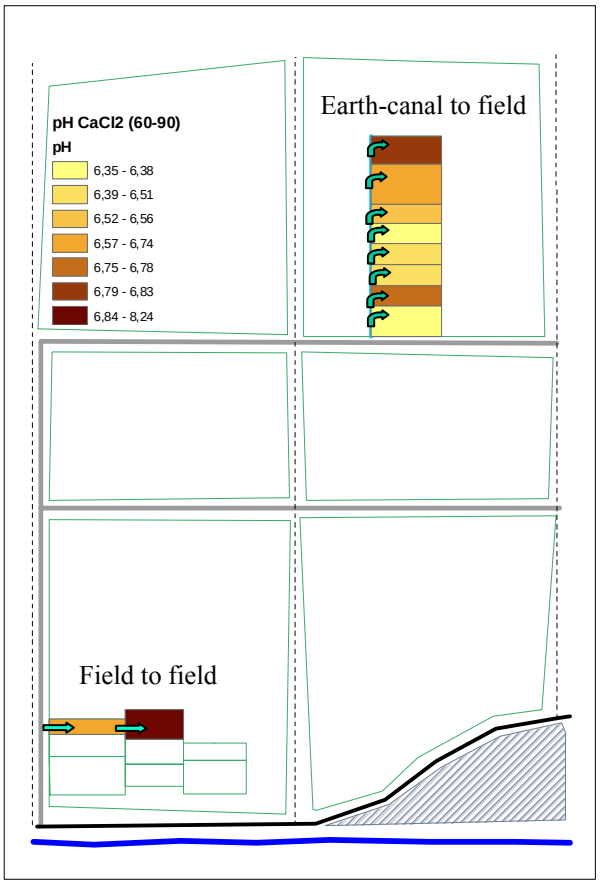

Fig. A3:6. pH in the soil layer 60-90cm

Appendix 4. Analytical data for soil and sediment samples

Table A4:1. EC, pH_{H2O} and pH_{CaCl2} in soil and sediment samples

Sample	depth	EC (uS/cm)	pH (H_2O)	pH (CaCl2)	mean depth	gradient	field
62	0-2	335,1	7,43	6,94	1	SeG4	1
1	0-15	80,94	6,55	5,85	7,5	SG2	1
2	15-30	51,89	8,01	6,69	22,5	SG2	1
3	30-60	49,46	8,1	6,75	45	SG2	1
4	60-90	42,44	7,77	6,38	75	SG2	1
63	0-2	163,3	7,59	6,83	1	SeG4	2
5	0-15	92,99	6,3	5,56	7,5	SG2	2
6	15-30	58,37	8,08	6,96	22,5	SG2	2
7	30-60	48,6	8,3	6,99	45	SG2	2
8	60-90	40,99	8,19	6,78	75	SG2	2
64	0-2	160	6,64	5,94	1	SeG4	3
9	0-15	85,3	6,77	6,02	7,5	SG2	3
10	15-30	56,45	7,91	6,81	22,5	SG2	3
11	30-60	45,88	7,92	6,72	45	SG2	3
12	60-90	37,16	7,79	6,5	75	SG2	3
65	0-2	174,6	7,06	6,28	1	SeG4	4
13	0-15	71,92	6,41	5,67	7,5	SG2	4
14	15-30	45,8	7,92	6,73	22,5	SG2	4
15	30-60	38,88	8,05	6,69	45	SG2	4
16	60-90	35,46	7,92	6,51	75	SG2	4
66	0-2	157	6,99	6,16	1	SeG4	5
17	0-15	57,72	6,5	5,68	7,5	SG2	5
18	15-30	39,67	7,83	6,55	22,5	SG2	5
19	30-60	37,39	7,94	6,61	45	SG2	5
20	60-90	33,29	7,65	6,35	75	SG2	5
21	0-15	58,59	6,64	5,91	7,5	SG2	6
22	15-30	45,2	7,88	6,71	22,5	SG2	6
23	30-60	39,88	7,87	6,65	45	SG2	6
24	60-90	34,7	7,79	6,56	75	SG2	6
25	0-15	54,82	6,32	5,41	7,5	SG2	7
26	15-30	43,45	7,77	6,6	22,5	SG2	7
27	30-60	40,74	8,18	6,93	45	SG2	7
28	60-90	30,59	8,12	6,74	75	SG2	7
29	0-15	50,69	6,29	5,37	7,5	SG2	8
30	15-30	45,82	7,95	6,75	22,5	SG2	8
31	30-60	43,75	8,12	6,88	45	SG2	8
32	60-90	32,71	8,2	6,83	75	SG2	8
53	0-2	421,3	5,79	5,47	1	SeG3	1
33	0-15	296,1	5,99	5,6	7,5	SG1	1
34	15-30	54,5	7,64	6,56	22,5	SG1	1
35	30-60	42,46	7,95	6,73	45	SG1	1
36	60-90	30,5	8,11	6,74	75	SG1	1
54	0-2	232,3	7,47	6,9	1	SeG3	2
37	0-15	338,5	6,1	5,73	7,5	SG1	2
38	15-30	88,68	7,36	6,55	22,5	SG1	2
39	30-60	46,01	7,9	6,79	45	SG1	2
40	60-90	33,72	8,24	6,92	75	SG1	2

Table A4:2. AqReg metal concentrations in soil and sediment samples

Sample	Cu ($mgkg^{-1}$)	Zn ($mgkg^{-1}$)	Cd ($mgkg^{-1}$)	Pb ($mgkg^{-1}$)	depth	gradient	field
62	18,3306	61,8795	0,1722	21,3412	0-2	SeG4	1
1	21,2472	63,5247	0,1408	24,0732	0-15	SG2	1
2	18,6798	66,9898	0,1231	21,4040	15-30	SG2	1
3	21,5425	76,8465	0,1174	22,5499	30-60	SG2	1
4	21,3225	72,2116	0,1338	20,2010	60-90	SG2	1
63	23,1241	67,3033	0,1741	25,5651	0-2	SeG4	2
5	23,8909	63,3052	0,1219	25,9499	0-15	SG2	2
6	20,3519	72,5668	0,1188	22,6419	15-30	SG2	2
7	20,2038	72,5066	0,1370	19,8866	30-60	SG2	2
8	19,9071	66,8841	0,1260	18,7258	60-90	SG2	2
64	22,2685	63,6787	0,1647	26,0193	0-2	SeG4	3
9	20,3356	59,6159	0,1048	23,4282	0-15	SG2	3
10	18,2101	65,2707	0,1368	20,4004	15-30	SG2	3
10R	19,0788	67,9501	0,1379	20,7534			
11	19,0617	69,3119	0,1073	18,9574	30-60	SG2	3
12	17,3869	60,5675	0,0972	15,5751	60-90	SG2	3
65	26,8939	78,8803	0,2269	28,7655	0-2	SeG4	4
13	21,2419	60,5915	0,1022	24,4436	0-15	SG2	4
14	17,3102	60,3096	0,0723	19,5968	15-30	SG2	4
15	19,6826	73,0089	0,1444	19,7869	30-60	SG2	4
16	18,7907	68,9735	0,1260	17,2038	60-90	SG2	4
66	21,0678	64,1306	0,1599	25,3593	0-2	SeG4	5
17	21,0602	61,1008	0,0918	24,8699	0-15	SG2	5
18	18,5443	67,5851	0,0904	20,7433	15-30	SG2	5
19	17,4318	68,2543	0,1299	16,6493	30-60	SG2	5
20	14,7796	54,6538	0,0829	12,8547	60-90	SG2	5
20R	15,0073	56,4052	0,1051	13,1981			
21	19,6540	59,0241	0,0982	22,5055	0-15	SG2	6
22	18,5952	63,5911	0,1246	19,4116	15-30	SG2	6
23	18,2944	64,9302	0,1114	17,6858	30-60	SG2	6
24	16,3738	58,1163	0,1064	15,1651	60-90	SG2	6
25	20,0508	54,6246	0,0825	22,1669	0-15	SG2	7
26	18,3495	60,7461	0,1062	20,0818	15-30	SG2	7
27	18,2774	64,8659	0,1097	17,7045	30-60	SG2	7
28	16,4684	59,1856	0,1124	15,6080	60-90	SG2	7
29	21,1506	59,7812	0,0933	23,8358	0-15	SG2	8
30	19,4976	66,4225	0,1298	21,2578	15-30	SG2	8
30R	19,0543	66,4609	0,1184	19,5867			
31	20,0001	68,4129	0,1077	19,8942	30-60	SG2	8
32	15,1885	55,2018	0,0881	13,9465	60-90	SG2	8
53	19,3171	76,1314	0,4201	21,8537	0-2	SeG3	1
33	20,4194	72,0942	0,2627	21,9033	0-15	SG1	1
34	22,0720	73,7493	0,1258	21,1901	15-30	SG1	1
35	20,4809	69,5575	0,1180	19,6980	30-60	SG1	1
36	19,4702	66,7983	0,1134	17,5890	60-90	SG1	1
54	20,1823	72,5382	0,2467	25,8908	0-2	SeG3	2
37	20,6809	71,7818	0,2027	25,5689	0-15	SG1	2
38	24,4328	76,5633	0,1725	23,4778	15-30	SG1	2
39	23,6116	80,7120	0,1663	22,6328	30-60	SG1	2
40	16,5844	58,5479	0,0929	15,3406	60-90	SG1	2

Table A4:3. Exchangeable metal concentrations in soil and sediment

Sample	Cu ($mgkg^{-1}$)	Zn ($mgkg^{-1}$)	Cd ($mgkg^{-1}$)	Pb ($mgkg^{-1}$)	depth	gradient	field
62	0,2018	0,0211	0,0018	<0,0004	0-2	SeG4	1
1	0,0126	0,2008	0,0063	0,0059	0-15	SG2	1
2	0,0058	0,0305	0,0008	0,0027	15-30	SG2	1
3	<0,0004	0,0961	0,0011	0,0006	30-60	SG2	1
4	<0,0004	0,0706	0,0041	0,0033	60-90	SG2	1
63	0,0761	0,0105	0,0012	<0,0004	0-2	SeG4	2
5	0,0045	0,3267	0,0072	0,0061	0-15	SG2	2
6	0,0102	0,1528	0,0007	0,0015	15-30	SG2	2
7	<0,0004	0,0236	0,0009	0,0005	30-60	SG2	2
8	<0,0004	0,0420	0,0014	<0,0004	60-90	SG2	2
64	0,0125	0,0835	0,0028	0,0007	0-2	SeG4	3
9	0,0113	0,2015	0,0033	0,0015	0-15	SG2	3
10	0,0039	0,0491	0,0009	0,0012	15-30	SG2	3
10R	0,0046	0,0428	0,0007	0,0006			
11	0,0015	0,0391	0,0008	0,0004	30-60	SG2	3
12	0,0030	0,0542	0,0025	0,0006	60-90	SG2	3
65	0,0852	0,0465	0,0018	0,0006	0-2	SeG4	4
13	0,0134	0,2443	0,0046	0,0055	0-15	SG2	4
14	<0,0004	0,0092	0,0006	<0,0004	15-30	SG2	4
15	<0,0004	0,0186	0,0008	<0,0004	30-60	SG2	4
16	<0,0004	0,0422	0,0017	<0,0004	60-90	SG2	4
66	0,0737	0,0460	0,0020	0,0014	0-2	SeG4	5
17	0,0076	0,2036	0,0048	0,0055	0-15	SG2	5
18	<0,0004	0,0407	0,0007	0,0003	15-30	SG2	5
19	<0,0004	0,0205	0,0007	<0,0004	30-60	SG2	5
20	<0,0004	0,0292	0,0027	0,0005	60-90	SG2	5
20R	<0,0004	0,0350	0,0027	0,0013			
21	0,0091	0,0924	0,0033	0,0024	0-15	SG2	6
22	0,0006	0,0089	0,0004	<0,0004	15-30	SG2	6
23	<0,0004	0,0109	0,0009	<0,0004	30-60	SG2	6
24	<0,0004	0,0266	0,0018	<0,0004	60-90	SG2	6
25	0,0095	0,3817	0,0073	0,0103	0-15	SG2	7
26	0,0010	0,0183	0,0007	<0,0004	15-30	SG2	7
27	<0,0004	0,0117	0,0006	<0,0004	30-60	SG2	7
28	<0,0004	0,0249	0,0012	<0,0004	60-90	SG2	7
29	0,0051	0,5590	0,0078	0,0165	0-15	SG2	8
30	<0,0004	0,0217	0,0005	<0,0004	15-30	SG2	8
30R	0,0006	0,0573	0,0004	<0,0004			
31	<0,0004	0,0084	0,0003	<0,0004	30-60	SG2	8
32	<0,0004	0,0156	0,0006	<0,0004	60-90	SG2	8
53	0,0301	0,2226	0,0155	0,0004	0-2	SeG3	1
33	0,0050	0,3667	0,0293	0,0018	0-15	SG1	1
34	<0,0004	0,0248	0,0028	<0,0004	15-30	SG1	1
35	<0,0004	0,0251	0,0027	<0,0004	30-60	SG1	1
36	<0,0004	0,0317	0,0020	<0,0004	60-90	SG1	1
54	0,0777	0,0286	0,0013	<0,0004	0-2	SeG3	2
37	0,0050	0,2345	0,0095	0,0012	0-15	SG1	2
38	0,0090	0,0521	0,0039	<0,0004	15-30	SG1	2
39	0,0014	0,0203	0,0024	<0,0004	30-60	SG1	2
40	<0,0004	0,0161	0,0011	<0,0004	60-90	SG1	2

Table A4:4. EC, pH_{H2O} and pH_{CaCl2} in sediment samples

Sample	EC (uS/cm)	pH	pH CaCl2	gradient	field
53	421,3	5,79	5,47	SeG3	1
54	232,3	7,47	6,9	SeG3	2
55	184,7	6,9	6,2	SeG3	3
56	489,7	5,74	5,42	SeG2	1
57	315,5	8,14	7,59	SeG2	2
58	381,1	6,11	5,67	SeG2	3
59	372,1	6,45	6,01	SeG1	1
60	1324	6,22	6,06	SeG1	2
61	281,4	7,06	6,56	SeG1	3
62	335,1	7,43	6,94	SeG4	1
63	163,3	7,59	6,83	SeG4	2
64	160	6,64	5,94	SeG4	3
65	174,6	7,06	6,28	SeG4	4
66	157	6,99	6,16	SeG4	5

Table A4:5. AqReg metal concentrations in sediment samples

Sample	Cu ($mgkg^{-1}$)	Zn ($mgkg^{-1}$)	Cd ($mgkg^{-1}$)	Pb ($mgkg^{-1}$)	gradient	field
53	19,3171	76,1314	0,4201	21,8537	SeG3	1
54	20,1823	72,5382	0,2467	25,8908	SeG3	2
55	25,9782	86,6558	0,3374	30,7649	SeG3	3
56	21,3882	80,1517	0,3915	25,2486	SeG2	1
57	22,6442	79,6618	0,3415	28,4965	SeG2	2
58	26,5279	86,7384	0,2266	31,7046	SeG2	3
59	22,3992	86,3360	0,4492	25,4668	SeG1	1
60	26,2609	93,4796	0,3709	29,8420	SeG1	2
61	26,5430	93,2742	0,2704	31,7301	SeG1	3
61R	27,9135	96,5305	0,2833	33,2159		
62	18,3306	61,8795	0,1722	21,3412	SeG4	1
63	23,1241	67,3033	0,1741	25,5651	SeG4	2
64	22,2685	63,6787	0,1647	26,0193	SeG4	3
65	26,8939	78,8803	0,2269	28,7655	SeG4	4
66	21,0678	64,1306	0,1599	25,3593	SeG4	5

Table A4:6. Exchangeable metal concentrations in sediment samples

Sample	Cu ($mgkg^{-1}$)	Zn ($mgkg^{-1}$)	Cd ($mgkg^{-1}$)	Pb ($mgkg^{-1}$)	gradient	field
53	0,0301	0,2226	0,0155	0,0004	SeG3	1
54	0,0777	0,0286	0,0013	<0,0004	SeG3	2
55	0,0360	0,0552	0,0028	<0,0004	SeG3	3
56	0,0062	0,8695	0,0261	0,0037	SeG2	1
57	0,1389	0,0158	0,0012	<0,0004	SeG2	2
58	0,0156	0,1389	0,0038	0,0004	SeG2	3
59	0,0187	0,1900	0,0098	<0,0004	SeG1	1
60	0,0331	0,2117	0,0052	<0,0004	SeG1	2
61	0,0285	0,0481	0,0016	<0,0004	SeG1	3
61R	0,0281	0,0532	0,0017	<0,0004		
62	0,2018	0,0211	0,0018	<0,0004	SeG4	1
63	0,0761	0,0105	0,0012	<0,0004	SeG4	2
64	0,0125	0,0835	0,0028	0,0007	SeG4	3
65	0,0852	0,0465	0,0018	0,0006	SeG4	4
66	0,0737	0,0460	0,0020	0,0014	SeG4	5